

# THE DISINFECTION OF PUBLIC WATER SUPPLIES WITH ELEMENTAL IODINE

By  
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The water in two water systems supplying three Florida correctional institutions and serving a total of approximately 800 individuals has been continuously disinfected with iodine for a period of two years under carefully planned chemical, bacteriological and medical controls.

The physical and chemical properties of iodine make it particularly suitable for use as a water disinfectant. Although its water solubility is not high, its saturated solution is sufficiently concentrated for feeding purposes. Its low chemical reactivity, least of all the halogens, means that lower residuals are more stable in the presence of organic or other oxidizable material, and the possibility of the production of tastes and odors by such reactions is minimized. No difficulties have been encountered in continuously feeding the element in saturated water solution to provide any desired dosage with an overall accuracy of plus or minus .05 parts per million.

Of over 1000 samples collected from the two systems for bacteriological analysis during a 22-month period of iodination, only about 2% were unsatisfactory.

Medical studies included the assessment of the three indices of thyroid function, namely, radioactive iodine uptake (RAI), protein bound iodine (PBI) and serum thyroxine ( $T_4$ ). Each subject received the series of tests twice before iodine feed was begun and 30 days apart, following which the tests were made on all subjects one, three, seven, and ten months after beginning the feed of iodine. The RAI intake dropped from about 17% at the beginning of the study to about 2% at the end. Values for PBI increased somewhat but the mean for the group was still within the range of values found in normal individuals. No significant change in the mean value for serum thyroxine was found. There has been no apparent change in the physical examination and in the size of the thyroid gland. No allergic reactions attributable to iodine have been found. There is no evidence to date that iodine under these experimental conditions has any detrimental effect on general health or thyroid function.

In dosages up to 1.00 parts per million, iodine produces no discernible color, taste, or odor in water.

A swimming pool study was made to investigate the possibility that iodine may be absorbed by the skin of individuals exposed to water containing it. Twenty-two subjects received the same series of tests as those used at Lowell before and after swimming throughout a period of one month in pool water disinfected with iodine. Average values for the group for RAI, PBI and  $T_4$  were not significantly changed and no evidence of allergy or change in size of the thyroid gland was detected in any subject during the study.

Both iodine and chlorine were shown to be effective disinfecting agents in the concentration range 0.3 - 0.6 parts per million and at pH values between 7.3 - 7.6. It is in the disinfection of swimming pool water that the ability to readily reoxidize and reuse the iodide ion pays greatest dividends. In this study a careful record was kept of all chemicals used for disinfection and pH control and accurate data covering disinfection were available. It was found that whereas the cost of chlorine disinfection had averaged \$7.98 per day, the cost for disinfection with iodine was \$4.70 per day. It is possible to disinfect swimming pool water with iodine at a cost approximately half that of chlorine.

These studies indicate that iodine is fully as effective as chlorine for the disinfection of public water supplies and that it possesses a number of advantages over chlorine when used for that purpose.

## I. INTRODUCTION

Iodine possesses the highest atomic weight of the four halogens, is least soluble in water, is least hydrolyzed by it, has the lowest oxidation potential, and reacts least readily with organic compounds. These somewhat negative characteristics might at first sight appear to be limiting factors with respect to its use for the disinfection of water. Actually, however, just the reverse is the case because, taken collectively, they mean that low iodine residuals should be more stable and therefore persist longer in the presence of organic or other oxidizable material than corresponding residuals of any of the other halogens. The high chemical reactivity of chlorine and its ability to react with organic material by oxidation, by substitution, or by addition, constitutes perhaps the greatest drawback to its effectiveness for water disinfection. The ideal water disinfectant would be some material, weak chemically and unable to participate in such reactions but which, at the same time, would possess bactericidal, cysticidal, and viricidal properties equal to or superior to those of chlorine.

Although iodine, in aqueous or hydroalcoholic solutions has had official status in the U. S. Pharmacopoeia since 1830, and has been an essential item in the home medicine cabinet for more than a century, recognition of its remarkable properties as a water disinfectant has been very slow to develop.<sup>1,2,3</sup> It was not until 1953 that Chang and

Morris<sup>4,5</sup> published their important studies of its effectiveness against bacteria, viruses, and cysts of *E. hystolytica*. Their studies were primarily responsible for its adoption by the military for the disinfection of canteen water in the field. In 1959, Black, Lackey and Lackey<sup>6</sup> published the first study of its effectiveness for the disinfection of swimming pool water and this work, together with that of others,<sup>7,8,9</sup> resulted in its tentative approval in 1962 by the U. S. Public Health Service for swimming pool disinfection, with the proviso that the maximum concentration of iodine in all forms shall not exceed five parts per million. To date, its use for this purpose has been approved by the states of Ohio, Pennsylvania, Illinois, North Carolina, Georgia, Texas and, with certain limitations, by the states of Florida and California.

The next logical step in the development of iodine for water disinfection, indicated by the remarkable successes in the aforementioned studies, was to use iodine for the disinfection of a public water supply under careful chemical, bacteriological and physiological control. This study was designed and initiated under these conditions with the following primary objectives:

1. To demonstrate the effectiveness of iodine for the disinfection of public water supplies.
2. To determine the physiological effects of iodine on a human population.
3. To evaluate the chemistry and technology of iodine under actual conditions of practical water disinfection.

In order to accomplish these objectives and others, elemental iodine was and is being used to disinfect the public water supplies of three state correctional institutions. These institutions are The Forest Hill School for Girls, The Florida Correctional Institution for Women, and The Florida Correctional Institution, Male Unit, all of Lowell, Florida. Iodine was and continues to be used to disinfect the University of Florida olympic size swimming pool. The data and results from these studies and the laboratory studies carried out in conjunction with these applied studies are presented and described in the following pages. These data were obtained during the period February, 1963 to September, 1965.

## II. IODINE THE ELEMENT

Iodine has an atomic number of 53 and an atomic weight of 126.91. It is a halogen from Group VII of the periodic table. It is the only halogen that is a solid at room temperature. Its vapor pressure at 25°C is only 0.31 mm of mercury, while that of bromine is 215 mm and that of chlorine is 5300 mm of mercury. The word iodine is derived from the Greek word "ioeides" meaning "violet colored." Its principal valence numbers are: -1, +1, +3, +5, +7. Iodine is a simple element with one stable atomic species of mass number 127 and it has ten or more radioisotopes. Of these,  $I^{131}$  with a half life of 8.08 days is the most useful tracer.

Iodine is the 47th most abundant element in the earth's crust. It is widely distributed in nature, but only in very small concentrations. Sea water contains about 0.05 parts per million. Certain seaweeds can extract iodine from sea water and accumulate it. Laminaria may be 0.45 percent iodine on a dry weight basis. Fucus is the next best seaweed source of iodine. Other sources of iodine in commercial concentrations include sponges, coral, deep oil well waters, springs in California, Java, Russia, and Italy and in the caliche nitrate deposits of Chile, which are the world's major source of iodine at present. It is found in trace quantities in many lakes and rivers. Tables 1 and 2<sup>10</sup> give the concentration of iodine found in certain lakes and rivers in the United States. Table 3 presents like data for some water supplies

in Iraq.<sup>11</sup> These data show that although iodine is widespread in nature, its concentration is extremely low.

Table 1  
Iodine Content of Water from Four of the Great Lakes

Lake	Iodine Content, Parts Per Billion
Superior at Duluth, Minn.	0.01
Superior at Marquette, Mich.	0.02
Michigan at Milwaukee, Wis.	0.015
Michigan at Winnetka, Ill.	0.10
Michigan at Chicago, Ill.	0.12
Erie at Cleveland, Ohio	0.86
Ontario at Toronto, Canada	1.45
Average	0.37

Table 2

Iodine Content of Water from Some United States Rivers<sup>10</sup>

River	Iodine Content, Parts Per Billion
Mississippi at Minneapolis, Minn.	0.88
Mississippi at St. Paul, Minn.	0.83
Mississippi at St. Louis, Mo.	3.52
Mississippi at New Orleans, La.	7.70
Missouri at Kansas City	1.69
South Platte at Denver, Colo.	0.77
Scioto at Columbus, Ohio	0.21
Cumberland at Nashville, Tenn.	0.22
Susquehanna at Harrisburg, Pa.	0.23
James at Richmond, Va.	0.60
Potomac at Washington, D. C.	0.72
Oconee at Atlanta, Ga.	3.20
Average	1.71

Table 3  
Iodine Content of Water Supplies in Iraq<sup>11</sup>

Location of Supply	Iodine Content, Parts Per Billion
Mosul	3
Tell Afar	17.5
Baghdad	3.5
Dohuk	7
Akra	4

### III. LITERATURE SURVEY

Iodine was discovered in 1811 by Bernard Courtois while making nitrates for Napoleon's Army.<sup>12</sup> Courtois sent a sample to J. L. Gay-Lussac who named it "iode" from the Greek for "violet colored." Gay-Lussac studied iodine and prepared many of its compounds.

The first practical use of iodine was in medicine in Switzerland. Dr. Coindet<sup>13</sup> used tincture of iodine to cure goiter in Geneva, Switzerland in 1819. In 1839, Davies<sup>14</sup> used tincture of iodine for the treatment of wounds. Watson<sup>15</sup> used dilute iodine solution to treat gonorrhea in 1867. Davaine<sup>16</sup> was the first to demonstrate the sporicidal activity of iodine solutions in 1873 employing the spores of the anthrax bacillus.

During our American Civil War tincture of iodine was carried to the field and used in the treatment of battle wounds.

The French made an unsuccessful attempt to use iodine for water disinfection during World War I. They added a mixture of potassium iodide and potassium iodate to the water to be disinfected and the iodine was to be released by lowering the pH. However, the very low pH required presented difficulties and the trials were abandoned.

One of the earliest references to the use of iodine for the disinfection of drinking water in this country appeared in the Union Pharmaceutique in May of 1915.<sup>17</sup> Five drops per liter of a solution consisting of 1 g of iodine, .05 g of potassium iodide, 1 g of water

and 8 g of 95% ethyl alcohol was deemed sufficient to disinfect water for troops in the field.

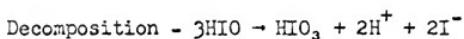
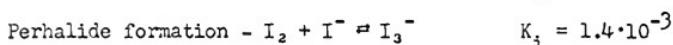
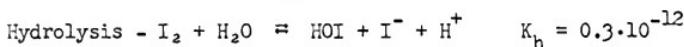
In 1922, Major A. P. Hitchens<sup>18</sup> of the Army Medical School stated that polluted water is rendered "safe for drinking" by adding "one drop of tincture of iodine to a canteen or a one-quart thermos bottle full of water." The Iodine Tincture Official at this time contained 7% free iodine and 5% potassium iodide.

In 1933, Beckwith and Moser<sup>19</sup> made what appears to be the first attempt to evaluate the bactericidal effectiveness of chlorine, bromine and iodine against soil bacteria and *E. coli*. They found that all three halogens killed from 88 to 99.9% of the organisms, in populations ranging from 2100-48,000 per ml, at dosages ranging from 0.5-2.0 ppm. They found that bromine was most effective, with iodine second and chlorine the least effective of the three. However, their methods for determining halogen residuals left much to be desired, chlorine and bromine residuals were determined with orthotolidine and color standards. Iodine dosages were calculated from initial concentrations and residuals were not determined. pH values, now recognized as critical factors, were not given and the results actually demonstrated little more than the fact that all three halogens possess bactericidal activity against the organisms studied.

In 1937, Pond and Willard<sup>20</sup> concluded that tincture of iodine 7% (U.S.P.) in a concentration of two drops per liter will ordinarily be sufficient to render any potable water innocuous within fifteen minutes. This 7% tincture of iodine also contained 5% potassium iodide.

Krabauskas, Harrington and Lauter<sup>21</sup> tested the effectiveness of iodine for the disinfection of 25 raw waters using 7% iodine tincture as the disinfectant. Eight drops per quart achieved sterilization with 30 minutes contact time for all of the waters tested. The bacterial counts of the waters ranged from 50 to 86,000 per milliliter and the turbidities from 1.6 to 490 parts per million. The pH range was 6.6 to 7.8.

In 1944, Wyss and Strandskov<sup>1</sup> found that the bactericidal activity of iodine is not as dependent upon concentration as is that of chlorine. They found that the sporocidal activity of iodine was almost independent of pH value and that the addition of equimolar concentrations of ammonia, succinimide or p-toluenesulfonamide to the water at pH 7.0 did not alter the rate of destruction of *B. metiens* spores. They concluded that the sporocidal action of iodine at pH values ordinarily encountered is due primarily to the  $I_2$  present, but that HOI may exert some action at high pH values. They found that the sporocidal activity of iodine was affected to a greater extent by temperature than was the activity of chlorine. The following four equations were presented for the chemistry of iodine in aqueous solution:



The rate of iodate formation was found to depend upon pH, the HIO concentration and the particular buffer system employed.

Gershenfeld and Witlin<sup>2</sup> concluded that bactericidal efficiency

tests of the dilute halogens (1:5000) revealed that free iodine solutions displayed more effective antibacterial activity against the test bacteria than did chlorine or bromine at 37°*C* or 24°*C* either in the absence or presence of organic matter. The quantity of organic matter present due to the added culture medium probably was a contributing factor for these results.

Marks and Strandkov<sup>22</sup> concluded that the killing rates of bacterial spores for the hypohalous acids and probably for the molecular halogens decrease in the order: chlorine, bromine, iodine. It is not known how well this would apply to other microbiological forms even though this is the order of chemical reactivity in general. They compared the effect of concentration on the killing times at pH 7 and 25°*C* and found the order of effectiveness to be chlorine, iodine and bromine. The concentrations were plotted in equivalents and they explained their observations by assuming that under these conditions chlorine exists chiefly as hypochlorous acid and bromine entirely as hypobromous acid, whereas iodine is present as molecular iodine. On a weight concentration basis, iodine was considerably less active than chlorine although still more active than bromine.

Ficarra<sup>23</sup> reported on the use of aqueous solutions of iodine as skin antiseptics in 100 post-operative cases, in which there were no post-operative wound infections. Aqueous iodine fulfills one of the primary requisites of a skin disinfectant in that it kills bacteria in a reasonably short time.

Chambers, Kabler, Maloney and Bryant<sup>24</sup> conducted studies on the

use of iodine as a bactericide. The purpose of the investigation was to provide information which would assist in evaluating iodine as a bactericide for use in water treatment. The study was specifically designed to determine under controlled conditions, the degree to which the bactericidal action of iodine is influenced by variations in exposure time, concentration, pH and temperature. They measured the bactericidal effectiveness of iodine against two strains of *E. coli*, three strains of *E. typhosa*, three other species of *Salmonella*, three different species of *Shigella*, *A. aerogenes* and *Streptococcus faecalis*. They concluded that the minimum average iodine concentration which kills all tested species in one minute under the most favorable conditions of pH (pH 6.5) and temperature ( $20^{\circ}\text{C}$  to  $26^{\circ}\text{C}$ ) is 0.60 parts per million. They found that *S. typhosa* was the least resistant to iodine and *S. sonnei* 1 was the most resistant of all cultures studied.

In May 1953, Chang and Morris<sup>4</sup> discussed elemental iodine as a disinfectant for drinking water. They reported that iodine is a suitable agent for the emergency disinfection of water supplies, for it is effective against all types of pathogenic organisms within a reasonable time at a concentration of a few parts per million. They attribute much of its effectiveness to its ability to maintain substantially constant germicidal efficiency in waters with high pH values and in waters containing ammonia or other nitrogenous impurities. They found that a dosage of eight parts per million of iodine gave complete destruction of 30 cysts (*E. hystolytica*) per ml within ten minutes in most natural waters, exceptions being waters with temperatures near  $0^{\circ}\text{C}$  or with iodine

demands greater than four parts per million. This same dose of iodine was found sufficient to reduce  $10^6$  enteric bacteria per ml to less than 5 per 100 ml within ten minutes and effective against leptospira, schistosomes and viruses. They concluded that its germicidal action is less dependent on pH, temperature, and time of contact than is that of chlorine, and that nitrogenous impurities do not impair its effectiveness, and side reactions leading to consumption of the germicide are less marked for iodine than for chlorinous disinfectants.

In 1953, Morris, Chang, Fair, and Conant<sup>5</sup> discussed water disinfection under field conditions. Their report included studies of several iodine-releasing compounds. They concluded that any of the iodine compounds discussed in this paper are suitable agents for the emergency disinfection of water supplies when used in amounts sufficient to yield eight parts per million of active iodine, and that the use of one tablet containing approximately 20 mg of tetraglycine hydroperoxide, 90 mg of disodium dihydrogen pyrophosphate, and 5 mg of talc per quart of water, is a convenient and reliable method for the emergency treatment of drinking water supplies.

In a study by the military,<sup>25</sup> Morgan and Karpen reported on the toxicology of low concentrations of iodine consumed in drinking water for extended periods under conditions of high humidity and temperature. Their principal objective was to discover any toxic effects of iodine consumed over a period of several months. They estimated that for the first 16 weeks of this study the average iodine intake per man per day was 12 mg. During the last ten weeks the iodine concentration in the

water was increased to provide an average estimated dose of 19.2 mg per man per day. The unique taste of the iodine treated water was first objectionable to most of the personnel, but after a period of exposure, only a few still found the taste unpalatable. The average values derived from serial clinical tests over the six-month period were compared with (a) conventionally accepted normal values, (b) average values from subjects consuming only chlorine treated water, and (c) each other to detect any significant pathologic trends. Symptoms, signs, and laboratory findings indicative of disease were sought in individual subjects.

Analysis of all the data failed to reveal evidence of weight loss, failure of vision, cardiovascular damage, altered thyroid activity, anemia, bone marrow depression, or renal irritation among the personnel consuming the iodinated water. In the opinion of the investigators, consumption of the iodinated water over a six-month period did not result in an unusual incidence of any form of skin disease. There was no evidence of sensitization to iodine among the healthy station personnel under observation, nor was there any indication of impaired wound healing or defective resolution of infections as a result of the consumption of iodinated water.

Witlin and Gershenfeld<sup>26</sup> tested iodine solutions against three organisms at three different temperatures ( $5^{\circ}\text{C}$ ,  $20^{\circ}\text{C}$ , and  $37^{\circ}\text{C}$ ). They tested iodine solutions by two different techniques against the organisms *E. Coli*, *M. pyogenes (aureus)* and *S. typhosa*, and concluded that in both instances, iodine was more effective than chlorine with

all three test bacteria at all three temperatures.

In 1957, Carroll, Iannarone, and Stonehill<sup>27</sup> in a presentation before the American Chemical Society discussed some of the chemical and antimicrobial properties of iodine solutions. They found that hypo-iodous acid was four to five times as effective as  $I_2$  against *M. pyogenes* (aureus) and three times as effective as  $I_2$  against *E. coli* (ATCC 9367). They found that HOI was more effective at halogenating proteins than  $I_2$ , and that HOI was a more effective protein denaturant than  $I_2$ .

Lawrence, Carpenter, and Nayler-Foote<sup>28</sup> studied iodophors and reported that the particular iodophor they studied (Wescodyne) was highly fungicidal, lethal to tubercle bacilli and effective against spores of *B. subtilis*.

Bartlett and Schmidt<sup>29</sup> reported on their study of surfactant-iodine complexes as germicides. They found that exposure of  $10^4$  infectious doses of virus to a dilution of bactericide containing 75 parts per million available iodine completely inactivated polio virus within two minutes. They used types I, II, and III pathogenic polio.

In 1958, Chang<sup>30</sup> set forth important considerations in water disinfection with elemental iodine. He discussed the cysticidal and viricidal efficiencies of various species of iodine and stated that at a given temperature and a given concentration of *E. hystolytica* cysts, the minimum cysticidal residual  $I_2$  is a function of contact time. He showed that the viricidal residual  $I_2$  and contact time were inversely proportional. Equations were presented for computing the cysticidal residual  $I_2$  with a given contact time, and vice versa, at varying

temperatures, as well as others for computing the cysticidal residual iodine in  $I_2$  -  $I_3^-$  systems. He pointed out that efficient use of halogens and active halogen compounds as water disinfectants demands a clear understanding of their chemical reactions in dilute water solutions and the relative germicidal efficiency of each species of active members that may be formed in the solution. Since natural fresh waters rarely contain enough iodine to interfere, given the pH, temperature, and titrable iodine demand of the water, and the iodide content in the preparation of elemental iodine, it is relatively simple with the information presented to compute the dosage of the iodine preparation needed to treat the water adequately for drinking purposes.

Gershenfeld and Witlin<sup>31</sup> described studies concerned with the rate of kill of iodine solutions, chlorine solutions and quaternaries. Solutions of elemental iodine exhibited the most rapid rate of kill and were superior to those chlorine solutions and quaternaries tested. In general, iodine sanitizing solutions exhibited the same efficiency in ten seconds as in one minute when using concentrations of more than ten parts per million of free iodine.

Black, Lackey and Lackey<sup>6</sup> were the first to use iodine to disinfect eight outdoor swimming pools. They reported iodine to be fully effective in the disinfection of the water of the eight swimming pools treated. It was not only equal to chlorine but in many cases superior. They found that iodine residuals were much less dependent upon bather load than chlorine residuals. This they felt, might be expected because iodine does not form substitution compounds with ammonia as does

chlorine. They found that no odors or tastes or irritations of the eyes of bathers were produced by the iodine residuals employed during the course of these studies, and no visible growths of algae were noted during the testing period.

In 1959, Black, Boudet, and Giddens,<sup>32</sup> in a second study, presented data on the use of iodine for swimming pool water disinfection which confirmed earlier data. Iodine was found to be an effective agent for the disinfection of swimming pool waters. They used four swimming pools and found no iodate build-up in the pH range 7.2-7.5. Iodine produced less change in pool pH than either chlorine or hypochlorite, whether fed as iodine-iodide solution, aqueous iodine solution, or iodine released from pool iodide by chlorine feed.

In 1960, Marshall, McLaughlin and Carscallen<sup>7</sup> reported their findings after iodination of a cooperative pool. Ninety-six percent of the tested samples conformed to drinking water standards. Due to a decrease in eye irritation, and despite the noticeable color changes, a majority of bathers (68.3%) preferred iodine-treated water to chlorine-treated water. No difficulties were encountered in the operation of an iodine disinfected pool with maintenance of free iodine in the range of 0.2 to 0.6 parts per million. The reactions of the operating personnel were unanimously favorable for iodine disinfection.

In 1961, Marshall, Wolford and Faber<sup>33</sup> reported the identity of an organism comprising 99% of the colonies appearing on standard plates in an iodine disinfected pool. They found that this organism was highly resistant to both chlorine and iodine. They concluded that apparently

alcaligenes faecalis has no great significance in the sanitary analysis of swimming pool water.

<sup>8</sup> Black summarized the properties of iodine which appear most attractive in swimming pool disinfection.

1. Use in a large number of swimming pools over extended periods of time has demonstrated its effectiveness as a germicide over a wide range of pH values.
2. It does not combine with ammonia to form iodoamines.
3. Its relatively low chemical activity makes it somewhat less dependent upon bathing loads and organic matter present in the water than other halogens.
4. Used in the form of HIO no color is produced in the pool water.
5. Odors and tastes are absent and irritation of the eyes of bathers does not appear to result from its use.

In 1961, Kabler, Clarke, Berg, and Chang<sup>34</sup> discussed the viricidal efficiency of disinfectants in water. They reported that iodine was an effective viricide, but required greater residuals and longer contact than hypochlorous acid. A greater contact time was of more benefit than increasing the concentration.

In 1962 it was reported<sup>35</sup> that 0.3 to 0.5 parts per million of both bromine and iodine inactivate at least six common enteroviruses, parainfluenza-1 virus and enteric bacteria.

Cothran and Hatlan<sup>9</sup> reported their results from iodine disinfection of an outdoor swimming pool. Their findings substantiated

previous findings. The pool required about 0.38 parts per million iodine per day. During the entire study, only two 24-hour standard plate counts were above 200 colonies per ml. Bathing load had little effect on water quality. The swimmers preferred the iodinated water because they had suffered eye burn the previous season when the pool was chlorinated.

In 1962, the Public Health Service<sup>36</sup> stated its position concerning the use of iodine for swimming pool waters and concluded that until more definitive information was available, iodine was an acceptable disinfectant for use in swimming pool waters provided the maximum concentration of iodine in all forms does not exceed five parts per million.

In 1963, Byrd, Malkin, Reed, and Wilson<sup>37</sup> reported the results of a study to determine the safety of iodine disinfection of swimming pools. They found no change in blood protein-bound iodine or urinary total iodine in 30 male subjects selected from three different swimming pools. The subjects were tested at one day, one week, and one month. They concluded that the use of iodine as a swimming pool disinfectant was safe, effective, and superior to the use of chlorine in regard to eye discomfort and irritation.

In 1964, Favero and Drake<sup>38</sup> compared the bacteriology of five swimming pools which were iodinated for a period of time and then chlorinated for a like period. They found there were fewer staphylococci, coliform bacteria, enterococci and streptococcus salivarius during the iodination period, but total viable counts were significantly high.

Iodine-resistant pseudomonads, physiologically identical to the non-pathogenic *alcaligenes faecalis*, were responsible for the high total viable counts.

Lackey, Lackey and Morgan<sup>39</sup> reported the algaecidal properties of iodine. They tested 136 species and found that 0.2 parts per million residual iodine gave good control, but not absolute kill, for in some instances cultures developed after standing for several weeks.

In 1964, a patent was granted to F. J. Zsoldos, Jr.<sup>40</sup> for a procedure for water treatment which utilizes chloramines plus hypoiodous acid to maintain a continuous disinfecting agent in a swimming pool.

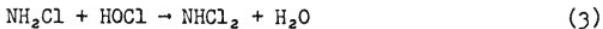
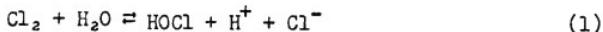
Berg, Chang, and Harris<sup>41</sup> reported on studies of the devitalization of microorganisms by iodine. They studied Poliovirus 1 (Lotshaw), Coxsackievirus A9, and Echovirus 7 with iodine dosages varying from 4.6 parts per million to 38.2 at pH 6. By extrapolation from their data, 99% devitalization of Coxsackie 49 virus required 1.27 parts per million iodine with 40 minutes contact at 25°C. Devitalization was described as the loss of the ability of a virion to reproduce itself. The validity of this extrapolation needs to be verified by actual experiment.

In 1965, Mills<sup>42</sup> studied the bactericidal properties of the halogens and reported that no sweeping general conclusions could be made regarding the relative activities of chlorine, bromine, and iodine. He found iodine more stable under ultraviolet light than either chlorine or bromine, and stated that much of the published literature was in disagreement on the relative activity of chlorine and

iodine, but there was little question that due to the larger detrimental effects of ammonia, pH and sunlight, chlorine in most practical cases was less effective. He concluded that physio-chemical factors influence the biocidal activity of the halogens and that comparisons of the biocidal activity of the halogens varied with the organisms under each specific set of conditions, and that knowledge of the factors influencing activity helped to determine the optimum conditions of disinfecting swimming pools.

#### IV. THE CHEMISTRY OF IODINE IN DILUTE AQUEOUS SOLUTION

In evaluating the effectiveness of any agent for the disinfection of water one must be familiar with all of the chemical reactions it is likely to undergo under actual conditions of use which means, of course, in very dilute aqueous solutions. For example, it has been shown that hypochlorous acid, HOCl, formed by the reaction of chlorine with water, is the most effective form of chlorine and that chloramines formed by the reaction of chlorine or hypochlorous acid with ammonia are much less effective.<sup>43</sup> These reactions are represented in equations one through four.



To illustrate the importance of the species of germicide present in dilute aqueous solution, Wattie and Butterfield<sup>44</sup> have shown that the ability of chloramines to destroy bacteria is far less than that of free available chlorine. These investigators demonstrated that in chlorine-free, chlorine demand-free water of pH 7.8 some *E. coli* survived after 120 minutes exposure to water containing 0.30 ppm of chloramine, and at pH 8.5 some *E. coli* survived for 240 minutes at the same chloramine concentration, namely, 0.30 ppm. In contrast, no *E. coli* survived after five minutes exposure to water containing only 0.07 ppm of free chlorine.

The statement is commonly made that free chlorine is approximately 30 times as effective as chloramines in bactericidal efficiency.

Effect of pH

In addition, hypochlorite ion,  $\text{OCl}^-$ , formed in increasing amounts as pH increases, is relatively ineffective in water disinfection. Equation (5) represents this equilibrium and Table 4, taken from the classical paper of Wattie and Butterfield<sup>44</sup> presents the percentage of each species at different pH values.



Table 4

Percent of Free Available Chlorine in the pH Range 4-10

pH	Molecular Chlorine	Hypochlorous Acid	Hypochlorite Ion
4	0.5	99.5	0
5	0	99.5	0.5
6	0	96.5	3.5
7	0	72.5	27.5
8	0	21.5	78.5
9	0	1.0	99.0
10	0	0.1	99.9

In the case of iodine, five different factors and four different substances must be considered.<sup>8</sup>

Hydrolysis of I<sub>2</sub>



$$\frac{[HIO][H^+][I^-]}{[I_2]} = K_h \quad (7)$$

$$K_h = 3 \times 10^{-13} \text{ at } 25^\circ\text{C} \text{ and } 9 \times 10^{-15} \text{ at } 0^\circ\text{C}.$$

Equation (6) represents the reaction of iodine with water to form hypoiodous acid, HIO, and the hydrolysis constant  $K_h$  is calculated from equation (7). Its value is  $3 \times 10^{-13}$  at  $25^\circ\text{C}$ . Chang<sup>30</sup> has calculated the effect of pH on this reaction for total iodine concentrations of from 0.5 to 50.00 parts per million. Table 5, calculated from his data for a total iodine residual of 0.5 parts per million, illustrates that whereas at pH 5 about 99% is present as elemental iodine and only 1% as hypoiodous acid, at pH 7 the two forms are present in almost equal concentrations, and at pH 8 only 12% is present as elemental iodine and 88% as hypoiodous acid. Both of these species are effective germicidal agents.

Table 5

Percent of I<sub>2</sub> Residual of 0.5 ppm Present

pH	I <sub>2</sub>	Hypoiodous Acid, HIO	Hypoiodite Ion, IO <sup>-</sup>
5	99	1	0
6	90	10	0
7	52	48	0
8	12	88	0.005

Effect of pH on Formation of Hypoiodite Ion

The second factor to be considered is the effect of pH on the conversion of hypoiodous acid,  $\text{HIO}$ , to hypoiodite ion,  $\text{IO}^-$ .



$$\frac{[\text{H}^+][\text{IO}^-]}{[\text{HIO}]} = K_a \quad (9)$$

$$K_a = 4.5 \times 10^{-13} \text{ at } 25^\circ\text{C}.$$

$$[\text{H}^+] = K_a \frac{[\text{HIO}]}{[\text{IO}^-]} \quad (10)$$

$$\frac{[\text{HIO}]}{[\text{IO}^-]} = \frac{[\text{H}^+]}{K_a} \quad (11)$$

Equation (9) is used to calculate the dissociation constant of hypoiodous acid,  $K_a$ , which is only  $4.5 \times 10^{-13}$  at  $25^\circ\text{C}$ . In other words,  $\text{HIO}$  is only very slightly stronger than pure water as an acid. With equation (11) it is readily possible to calculate for any hydrogen ion concentration and pH value the ratio of undissociated acid to hypoiodite ion. Equations (12) and (13) illustrate this for pH 8 and pH 9.

pH 8 at  $25^\circ\text{C}$ .

$$\frac{[\text{HIO}]}{[\text{IO}^-]} = \frac{1 \times 10^{-8}}{4.5 \times 10^{-13}} = 2.2 \times 10^4 \quad (12)$$

pH 9 at  $25^\circ\text{C}$ .

$$\frac{[\text{HIO}]}{[\text{IO}^-]} = \frac{1 \times 10^{-9}}{4.5 \times 10^{-13}} = 2.2 \times 10^3 \quad (13)$$

So at pH 8 there are 22,000 undissociated  $\text{HIO}$  molecules to each hypoiodite ion, and at pH 9 the ratio of  $\text{HIO}$  to  $\text{IO}^-$  is still 2200 to 1.

It is of interest to compare the effects of pH on chlorine and iodine residuals. When Tables 4 and 5 are compared, it will be noted

that whereas at pH 8.0, 78.5% of a chlorine residual is present as relatively ineffective hypochlorite ion and only 21.5% is present as hypochlorous acid, at the same pH, 88% of the corresponding iodine residual is present as hypoiodous acid, 12% as diatomic iodine, both effective germicides, and only 0.005% or an unmeasurable trace is present as hypoiodite ion. This is an important advantage of iodine over chlorine for water disinfection at high pH values.

#### Formation of Tri-iodide Ion, $I_3^-$

The third factor is the possibility of the formation of bactericidally ineffective tri-iodide ion,  $I_3^-$ . Equation (14) represents this reaction.



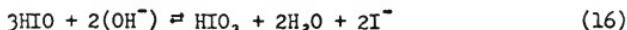
$$\frac{[I_2]}{[I_3^-]} \cdot \frac{[I^-]}{[I_2]} = K_i \quad (15)$$

$$K_i = 1.4 \times 10^{-3} \text{ at } 25^\circ\text{C} \text{ and } 0.7 \times 10^{-3} \text{ at } 0^\circ\text{C}.$$

Chang<sup>30</sup> investigated this reaction and has calculated that the formation of the tri-iodide ion will not be significant or even measurable at the low concentrations of  $I_2$  and  $I^-$  which would be present in water disinfected with iodine.

#### Formation of Iodate Ion

The fourth factor is the conversion of hypoiodous acid to iodate ion at high pH values, according to the following reaction.

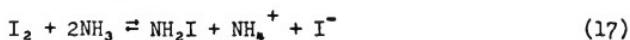


It has been shown that iodate ion possesses no disinfecting ability. Chang<sup>30</sup> found that an iodate solution capable of liberating 10,000 parts per million of titrable iodine in the presence of an acid and iodide exhibited no cysticidal effect at pH 7.0 and 25°C even after four hours contact time. Any substantial formation of iodate would, to the extent that it is formed, lower the disinfecting ability of the dosage of iodine added. Wyss and Strandskov<sup>1</sup> studied this reaction in carbonate, borate and phosphate buffers and found that at high pH values this reaction proceeds rapidly. According to their data the decomposition rate in a solution containing 30 parts per million or less titrable iodine is slow at pH 8.0 maintained by a borate or carbonate buffer, whereas in the presence of a phosphate buffer, two-thirds of the HIO has been converted to iodate in 40 minutes. At pH 9.0 the rate of decomposition was found by them to be so rapid that in ten minutes about two-thirds, three-fourths and five-sixths of the HIO was converted to iodate in borate, carbonate, and phosphate buffer, respectively. However, their work was done employing concentrations of hypoiodous acid and iodine, HIO and I<sub>2</sub>, in relatively high concentration, many times greater than would be encountered in water disinfection practice. Data to be presented in this study show conclusively that such reversion does not take place in the buffers used by them when concentrations of I<sub>2</sub> and HIO used in water treatment practices are employed.

No Reaction with Ammonia

The fifth factor to be considered is the question whether I<sub>2</sub> or

HIO will combine with ammonia or ammonia derivatives in water to form iodoamines. Strong solutions of iodine and ammonia will combine to form the very explosive compound NI<sub>3</sub>, but in the dilute aqueous solutions used in water disinfection practice there is no reaction between iodine and ammonia. McAlpine<sup>45</sup> gives evidence that a colorless iodoamine is found according to the following reaction.



$$K = \text{about } 2$$

He bases the validity of this reaction on the decolorization which takes place when 50 ml of 0.01 N KI<sub>3</sub> solution was added to 200 ml of 0.01 N NH<sub>3</sub>. Data to be presented in this study show that the possibility of iodoamine formation in dilute aqueous solution is extremely remote when concentrations of iodine which are used in water disinfection are used.

## V. RESEARCH PLAN AND EXPERIMENTATION

Based on the data obtained in previous studies, it was felt that the time had come to evaluate the effectiveness of iodine as a water disinfectant in broad perspective, and this study was therefore planned to demonstrate its effectiveness for the disinfection of public water supplies and to determine the physiological effects on a human population. In order to demonstrate these parameters and many others, a captive population of approximately 800 individuals consisting of white adult males and females and Negro women and girls was selected, and the water supplies involved were iodinated. The data presented in this study have been accumulated over a period of more than two years and actual iodination has been continuously carried out since October, 1963.

### Iodine Disinfection at Lowell, Florida

#### Description of Water Systems

Station No. 1 - Three institutions at Lowell, Florida, were selected as the site of this investigation because they duplicate institutional and municipal water systems and because their populations are maintained under controlled environmental conditions where they are available for physiological testing. Station No. 1 is the larger of the two water systems being used for this study and supplies the Florida Correctional Institution for Women, a maximum security prison, and the Forest Hill School for Girls, a school for delinquent Negro girls,

located on adjoining tracts at Lowell, Florida, about 27 miles distant from the University of Florida campus. Figures 1 and 2 are aerial photographs of the Women's prison and the School for Girls. Figures 3, 4 and 5 are schematics of all three institutions. This water system consists of two four-inch diameter wells approximately 150 feet deep, a 75,000 gallon covered ground storage reservoir, a high service pump station containing two 60 gallon per minute centrifugal pumps and one 500 gallon per minute fire service pump, and a 75,000 gallon elevated storage tank which floats on the distribution system. The pump house contains additional metering and chemical feeding equipment plus gasoline engines for stand by power. The daily demand of this system ranges between 70,000 gallons per day and 100,000 gallons per day, and it serves approximately 500 individuals, including inmates of the two institutions, administrative staff and civilian employees. Each institution has its own laundry facility. Figure 6 illustrates the original equipment in Station No. 1. Figure 7 presents the monthly water consumption at Station No. 1 for the period of this study through August, 1965.

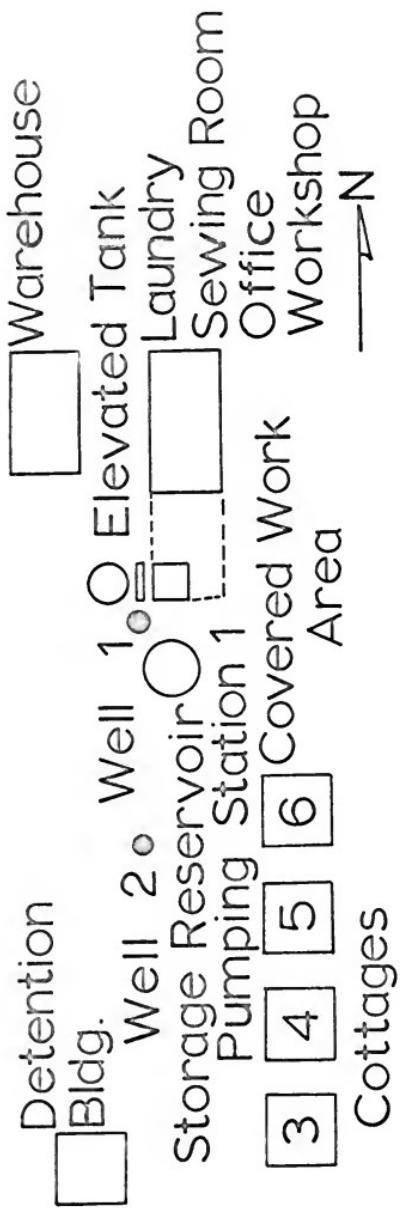
Station No. 2 - This station is the smaller of the two and supplies a men's medium security prison located about one mile distant from the others. It has one six-inch diameter well, a 4,000 gallon hydropneumatic tank, and a pump house containing high service metering and chemical feeding equipment. The daily demand of the smaller system ranges between 20,000-30,000 gallons per day and it serves approximately 180 inmates, administrative staff and civilian employees. Figure 8 shows the original equipment of Station No. 2. Figure 9 contains the



Fig. 1 - Aerial Photograph of the Florida Correctional Institution for Women.



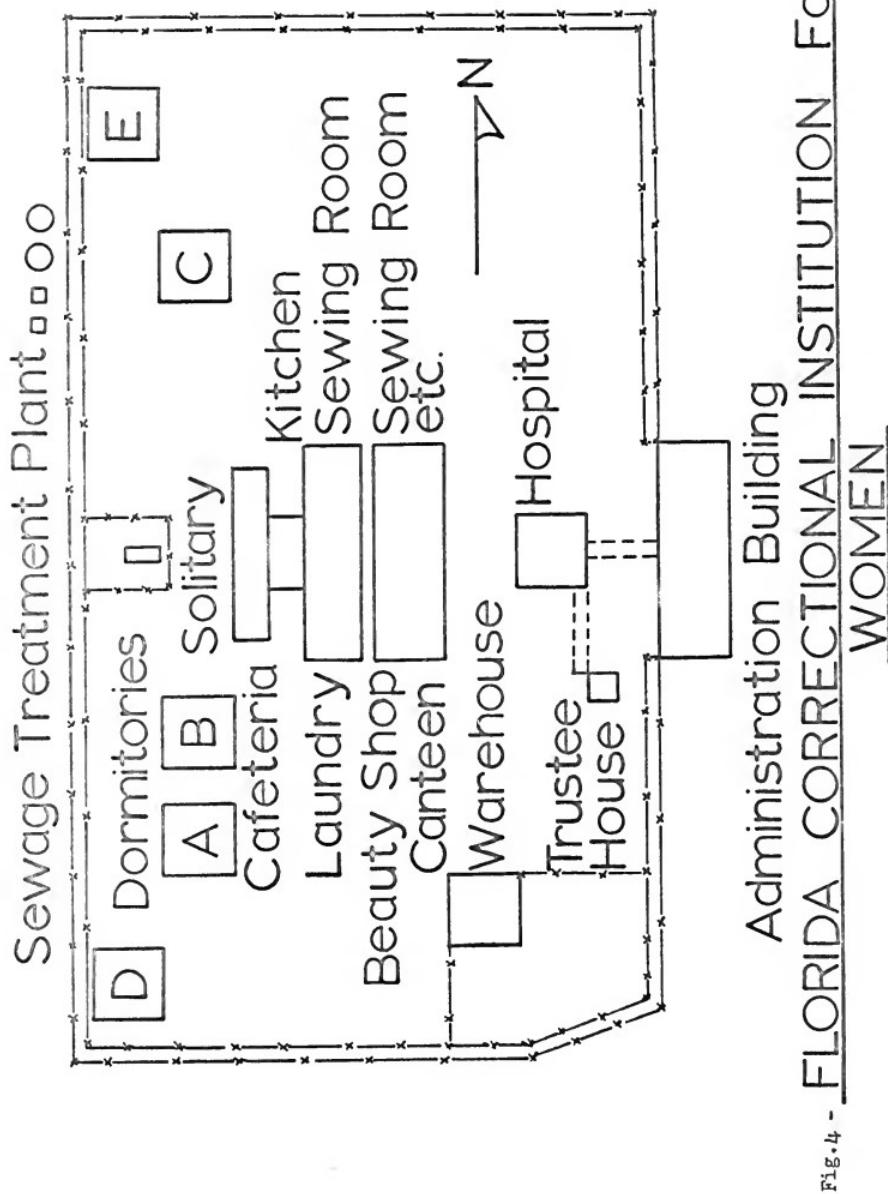
Fig. 2 - Aerial Photograph of the Forest Hill School for Girls.

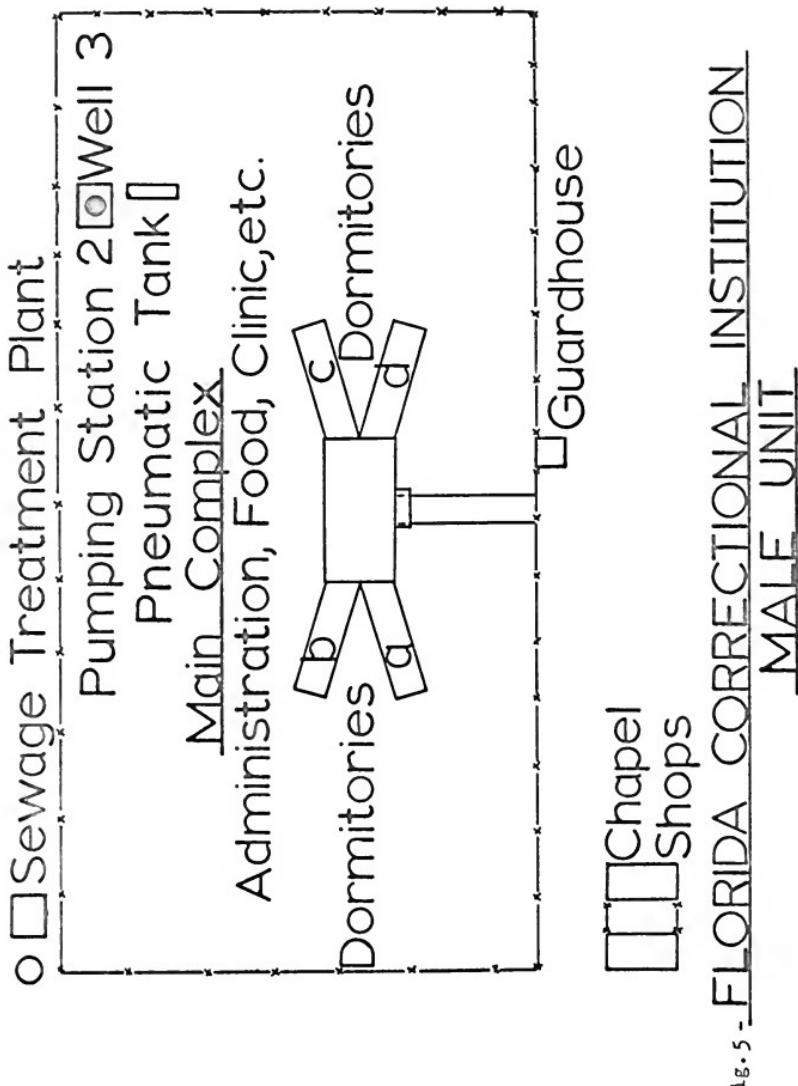


School Complex  
Classrooms,  
Clinic, Gym,  
Kitchen, Offices, etc.

Cottages  
7  
8  
9

Fig. 3 - FOREST HILL SCHOOL  
FOR GIRLS





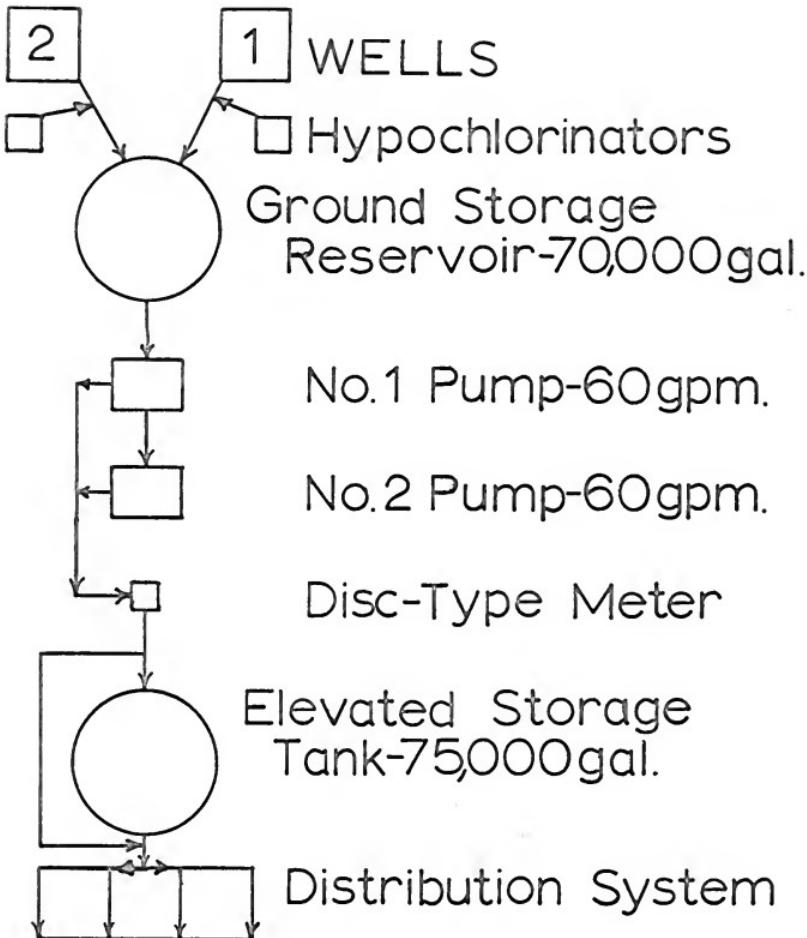
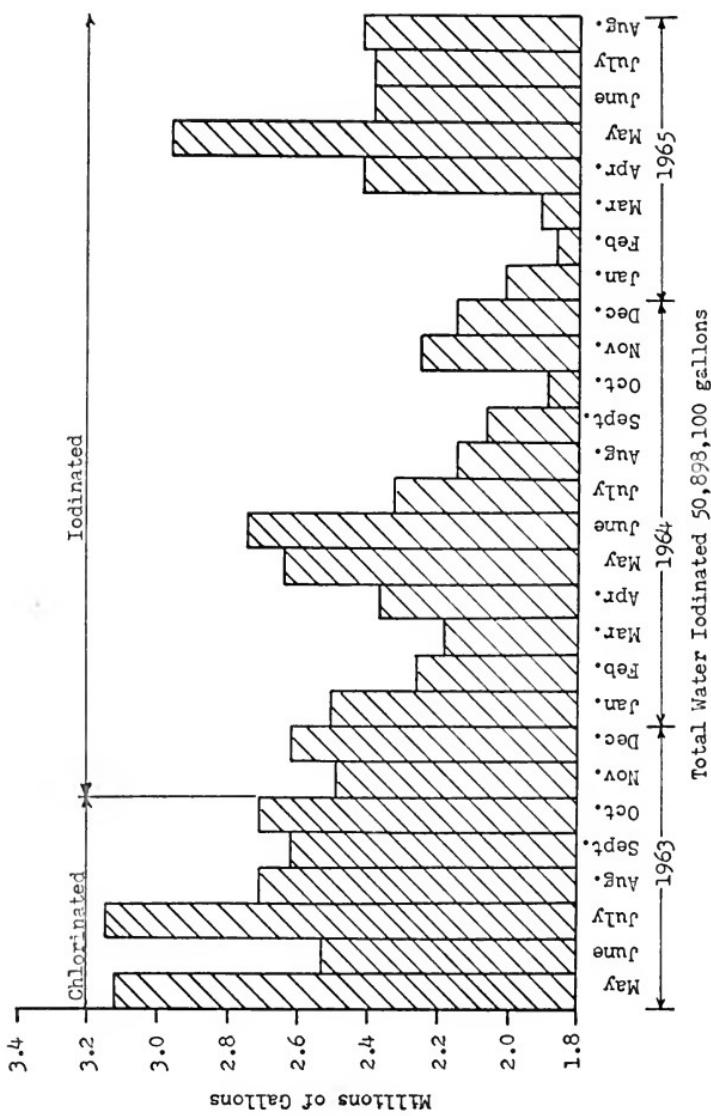
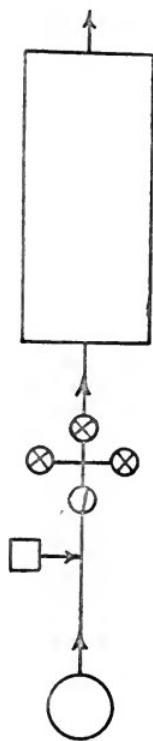


Fig. 6 - ORIGINAL WATER SYSTEM  
Women's Prison & Girls' School



Total Water Iodinated 50,893,100 gallons

Fig. 7 - Monthly Water Use at Station 1, May 1963 to September 1965.



Distribution System

Pneumatic Tank-4000gal.

3 Gate Valves

Check Valve

Hypochlorinator

Well & Pump-200gpm.  
On-30 Off-60psi.

Fig. 8 - ORIGINAL WATER SYSTEM  
Men's Prison

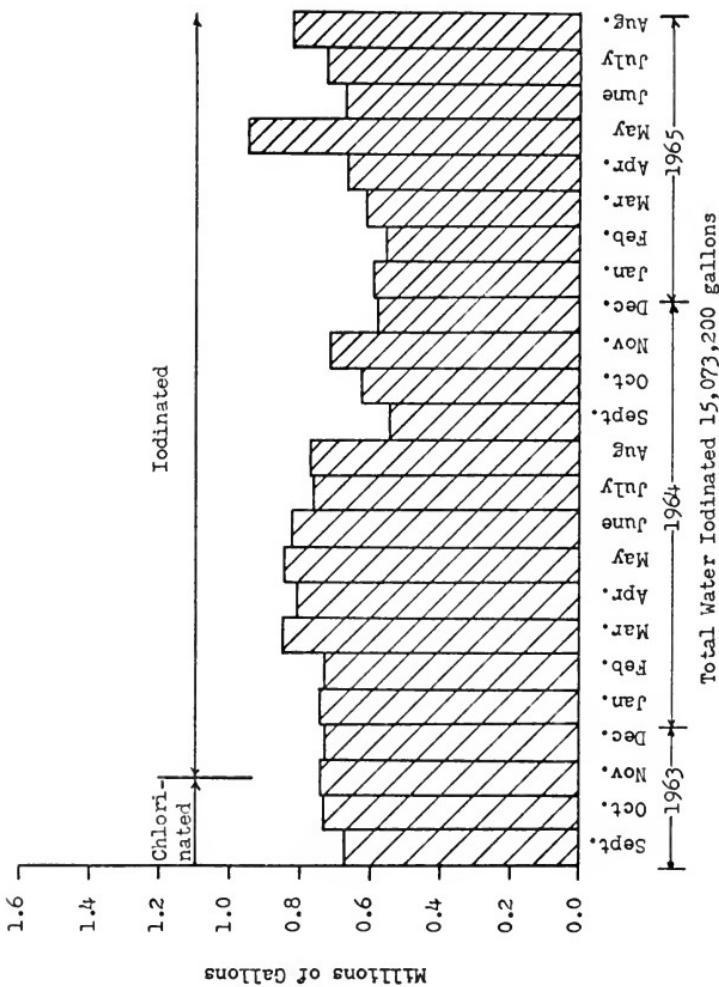


Fig. 9 - Monthly Water Use at Station 2, September 1963 to September 1965.

monthly water consumption data for this station for the period of the study through August, 1965. Table 6 contains the water consumption data for both stations for the entire period of the study. Prior to the initiation of this study, the water in both systems was being disinfected with calcium hypochlorite.

Chemical Characteristics of the Well Waters

The chemical characteristics of the water obtained from all three wells are typical of wells penetrating the limestone aquifer which underlie practically all of Florida. Individual chemical analysis of the three wells are shown in Table 7, and the results of the spectrographic determination of the concentration ranges of eight trace elements are shown in Table 8. A ten liter sample was evaporated to dryness for the trace analyses. The analyses indicate that the water is moderately hard, very low in iron and free from hydrogen sulfide. The organic content of the water is low and, as will be shown later, the bacteriological quality of water from Wells No. 1 and No. 2 has been found to be poor throughout the entire investigation, whereas the raw water from Well No. 3 meets the bacteriological criteria of the 1962 DRINKING WATER STANDARDS.<sup>46</sup> Coliform organisms have been present in more than 50% of samples collected from Well No. 2, and in about 30% of those from Well No. 1. It is unusual to characterize the presence of enteric organisms in a water supply as fortunate, but in this case it is fortuitous since it eliminates the necessity of adding some indicator organism or organisms to the water before disinfection.

Table 6

Lowell Water Consumption Data  
May 1963 to September 1965

Month	Station 1	Station 2
	Water Consumption (Gal.)	Water Consumption (Gal.)
May 1963	3,117,740	
June	2,525,940	
July	3,148,670	
August	2,710,000	
September	2,620,000	666,000
October	2,714,000	730,800
November	2,393,140	736,800
December	2,622,120	729,600
January 1964	2,508,860	740,400
February	2,260,320	732,000
March	2,182,560	852,000
April	2,374,730	806,400
May	2,642,190	844,800
June	2,745,950	820,800
July	2,319,840	760,800
August	2,154,100	771,600
September	2,057,730	537,600
October	1,894,750	615,600
November	2,249,780	709,200
December	2,152,600	574,800
January 1965	2,011,940	589,200
February	1,856,870	553,200
March	1,909,960	613,200
April	2,418,570	662,400
May	2,963,020	950,400
June	2,377,190	669,600
July	2,377,920	720,000
August	2,423,960	819,600

Total water iodinated through August, 1965 - 65,971,300 gallons.

Total for Station 1 - 50,898,100 gallons.

Total for Station 2 - 15,073,200 gallons.

Average daily consumption at Station 1 - 78,000 gallons.

Average daily consumption at Station 2 - 23,200 gallons.

Table 7  
Chemical Analyses of Water from Individual Wells

Constituent	Parts per million		
	Well No. 1	Well No. 2	Well No. 3
Total dissolved solids	229.	220.	230.
Silica, SiO <sub>2</sub>	12.	11.	11.
Iron, Fe	.01	.03	.05
Calcium, Ca <sup>++</sup>	71.	70.	64.
Magnesium, Mg <sup>++</sup>	8.0	7.3	7.5
Sodium and potassium, as Na <sup>+</sup>	2.0	2.0	2.0
Bicarbonate Ion, HCO <sub>3</sub> <sup>-</sup>	214.	215.	205.
Sulfate Ion, SO <sub>4</sub> <sup>=</sup>	4.5	5.2	6.5
Chloride Ion, Cl <sup>-</sup>	12.	11.	5.
Nitrate Ion, NO <sub>3</sub> <sup>-</sup>	0.61	0.55	2.2
Fluoride Ion, F <sup>-</sup>	0.20	0.10	0.10
Temp °C	21.5	21.5	21.5
pH	7.4	7.4	7.4

Table 8  
Trace Elements in Water from Well No. 1

Element	Concentration Range, ppb
Boron, B	2.3 - 23
Chromium, Cr	23 - 230
Copper, Cu	23 - 230
Manganese, Mn	23 - 230
Nickel, Ni	2.3 - 23
Strontium, Sr	23 - 230
Titanium, Ti	23 - 230
Silver, Ag	0.23 - 2.3

Iodination Procedure

Considerable renovation was necessary at Station No. 1 before iodination could begin. A new roof, a sump pump, new doors and an adequate drainage system were installed prior to iodination. Softening equipment and a compressor were removed from the pump house to allow space for the iodination equipment. The old disc-type meter was returned to the factory for overhaul and new impellers were installed in the pumps. New float switches were installed for the elevated tank so that the system would be completely automatic. Figures 10 and 11 show the station in its original condition and following its renovation. Station No. 2 required some piping changes and a new air relief valve.

and check valve, but since the Station is relatively new, less renovation was necessary here than at Station No. 1.

The Feeding of Elemental Iodine to Water

In this study iodine is being fed as the element in saturated aqueous solution, although in practice it may also be added in the form of a soluble iodide and then oxidized to the element by the addition of an appropriate oxidizing agent. This point will be referred to again in the laboratory studies section. The continuous accurate feed of iodine in the two water systems has been found to be remarkably simple. Although iodine is less soluble in water than any of the other halogens, its solubility is appreciable and is significantly temperature dependent. Figure 12 illustrates the change in concentration of a saturated aqueous solution from  $0^{\circ}\text{C}$  to  $60^{\circ}\text{C}$  in the absence of added iodide ion. The ground water has a temperature of  $21.5^{\circ}\text{C}$  which remains practically constant throughout the year. It was only necessary to equip the pump station with a heat pump so adjusted as to maintain the temperature within the station at  $21.5^{\circ}\text{C}$  to continuously produce a saturated iodine solution with a constant concentration of 305 parts per million. Saturation is achieved by passing some of the raw well water through a bed of elemental iodine crystals of sufficient depth for saturation to take place in what is called an iodine saturator. Figure 13 is a schematic of the iodine feed apparatus.

A cross section of the simple saturator employed at Station No. 1 for 22 months is shown in Figure 14. It is constructed of a five foot section of vitrified clay pipe with a reinforced concrete plug at the



Fig. 10 - Station No. 1 at the Beginning of the Project.



Fig. 11 - Station No. 1 with Iodination Equipment Installed.

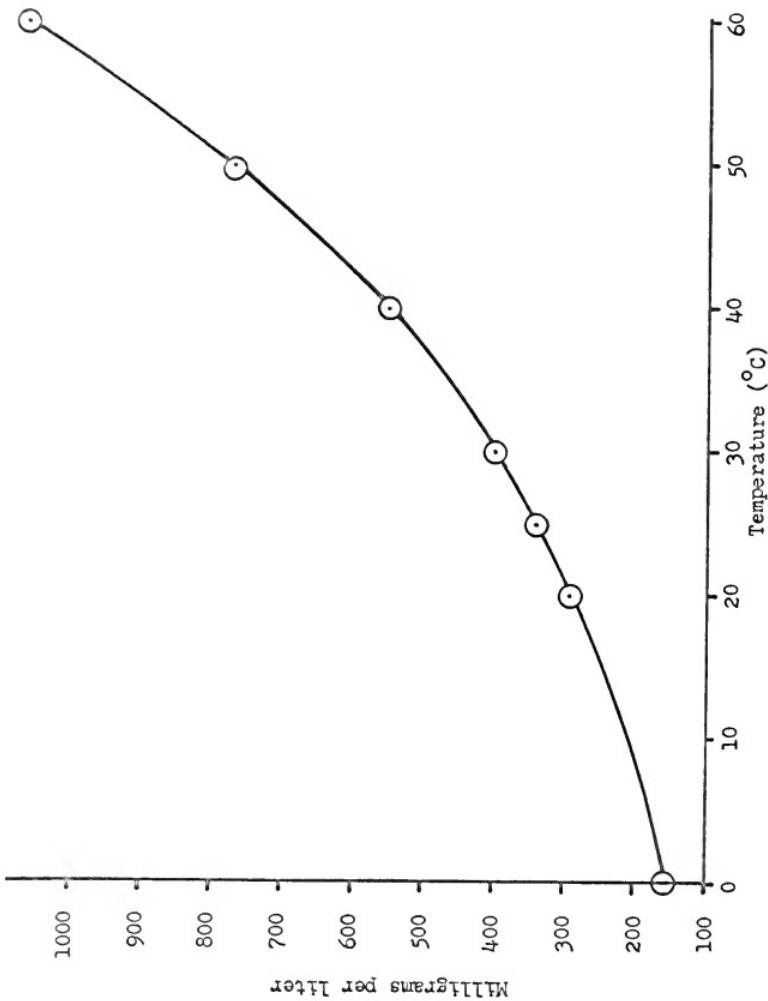


Fig. 12 - Iodine Solubility in Water.

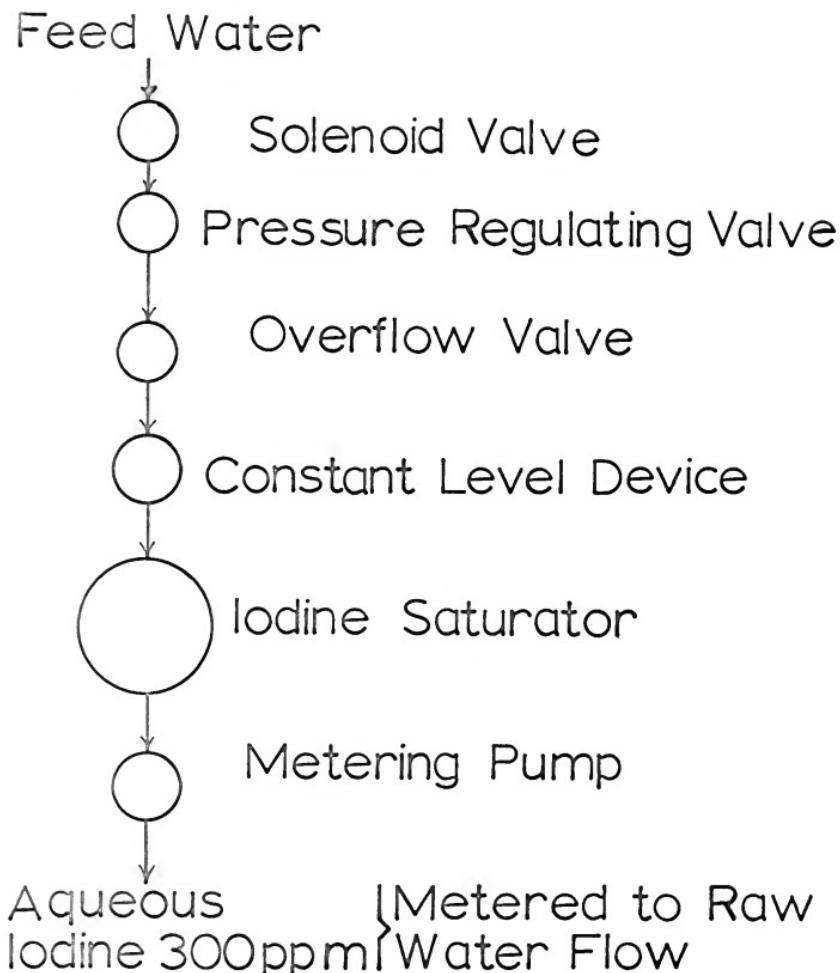


Fig. 13-IODINE FEED APPARATUS

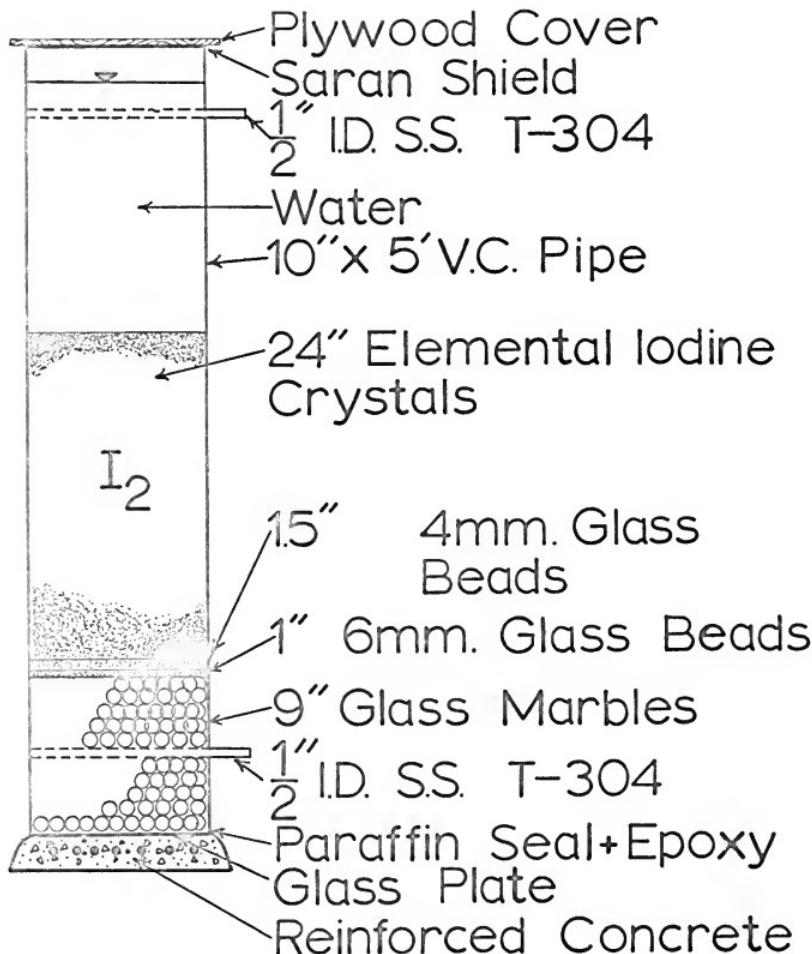


Fig.14 - IODINE SATURATOR  
Station 1

bottom. Above the plug is a one-fourth inch glass plate, a nine inch column of glass marbles, a one inch layer of six millimeter glass beads, a 1.5 inch layer of four millimeter glass beads, and 24 inches of technical grade elemental iodine crystals. Water passes through a small constant level tank mounted on the side of the saturator into the saturator about two inches below the top and downward through the bed of iodine crystals. A stainless steel pipe passing through the pipe wall into the glass marble section at the bottom of the saturator carries the saturated iodine solution to the metering pumps. The capacity of the pipe section is such that it is not necessary to employ additional storage for saturated iodine solution. The descending column of fresh water above the bed of crystals prevents the escape of any iodine vapor and the only cover provided for the saturator is a thin sheet of Saran and a plywood square to hold it in place. The addition of iodine to the saturator consists simply of removing the plywood cover and pouring the iodine crystals into the saturator. The saturated iodine solution is pumped from the saturator and metered very accurately against the raw water flow by means of stainless steel positive displacement metering pumps. Each of the stainless steel metering pumps is electrically interconnected to one of the high service pumps, and complete automation is provided by differential pressure gauges operated from the water level in the elevated storage tank. All pipe carrying saturated iodine solution is stainless steel or equivalent. Figure 15 is a photograph of the upper part of the saturator showing the constant level cylinder, needle valve and solenoid valve for

automatic operation, and Figure 16 shows the lower part of the saturator and the stainless steel lines carrying the iodine solution to and from the metering pumps.

Figure 17 is a schematic diagram of all the equipment and instrumentation at Station No. 1, and Figure 18 is a schematic diagram of the equipment at Station No. 2. With this equipment it has been possible to continuously feed saturated iodine solution to provide any desired dosage of iodine with an overall accuracy of  $\pm 0.05$  parts per million. During the 22 months which have elapsed since iodination was begun, and during which 65 million gallons of water have been iodinated, only two brief interruptions have occurred. Both of these interruptions of service were due to electrical failure of the solenoid valve because of overload and consequently the saturator could not make any iodine solution without water. Figure 19 shows the interior of Station No. 1 and Figure 20 is an aerial photograph of the Male Unit.

#### Chemical Control

Desired iodine residuals are monitored with a continuous iodine analyzer-recorder located inside the pump station and supplied with iodinated water from the high-service discharge line one minute after iodine injection. A second portable iodine analyzer-recorder is moved from place to place in the system and a continuous record of iodine residuals secured. During the first five months of iodination daily charts were used in both instruments. As soon as the overall accuracy of feeding had been established, both were adapted for the use of weekly charts. Figure 21 shows a typical daily chart, and Figure 22

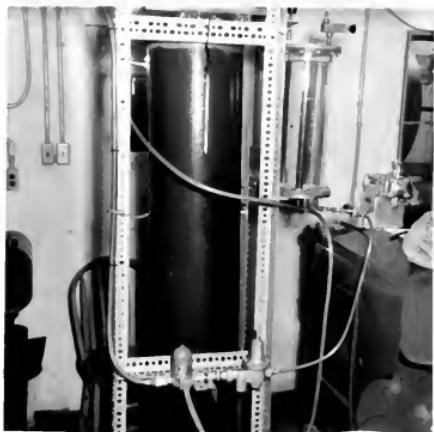


Fig. 15 - The Upper Portion of the Iodine Saturator in Station No. 1.



Fig. 16 - The Lower Portion of the Iodine Saturator in Station No. 1 with Adjacent Chemical Metering Pumps.

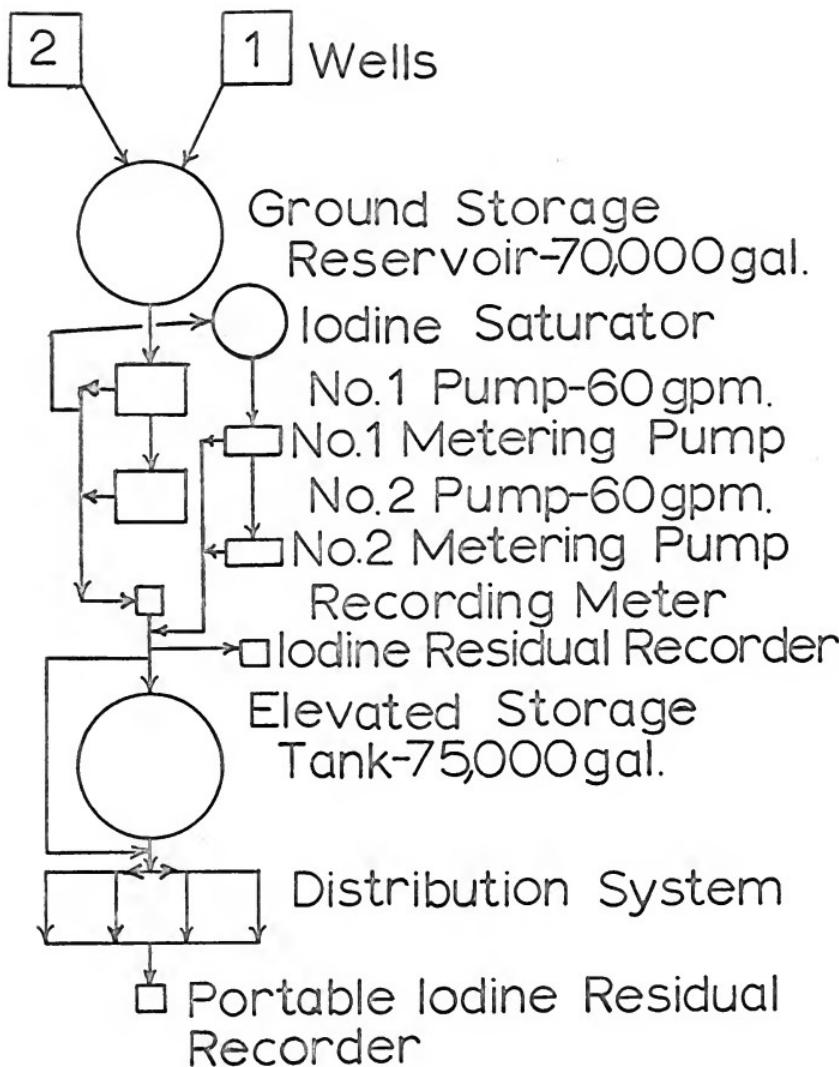


Fig. 17 - ADAPTED WATER SYSTEM  
Women's Prison & Girls' School

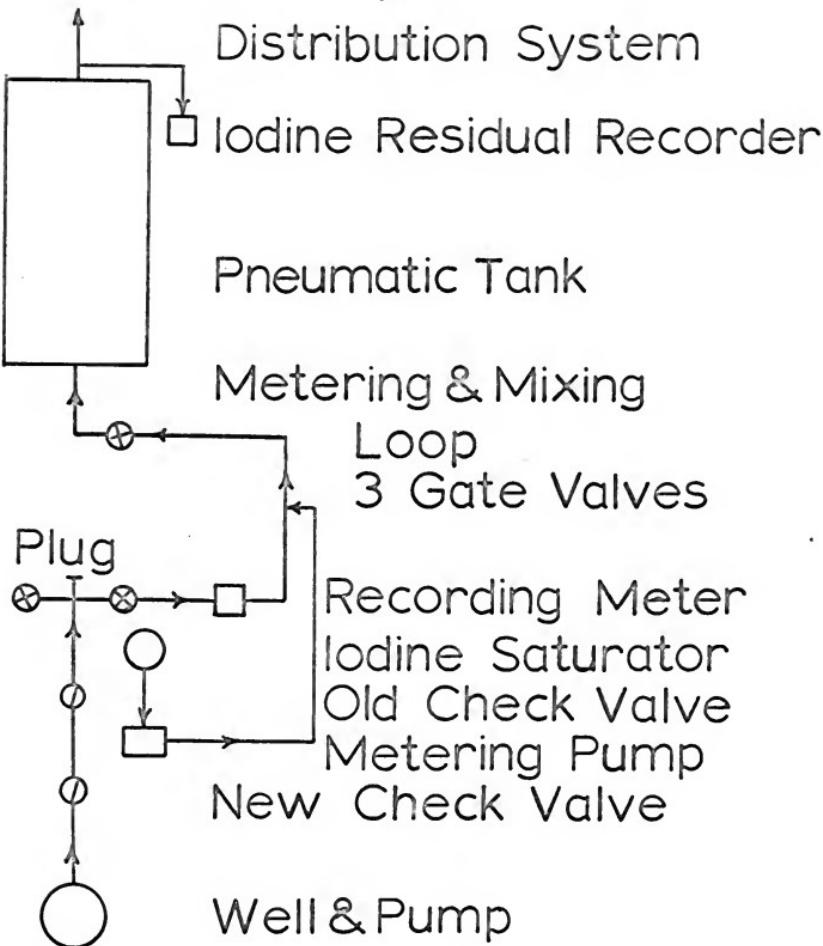


Fig. 18 - ADAPTED WATER SYSTEM  
MEN'S PRISON



Fig. 19 - Interior of Station No. 1.



Fig. 20 - Aerial Photograph of Male Unit.

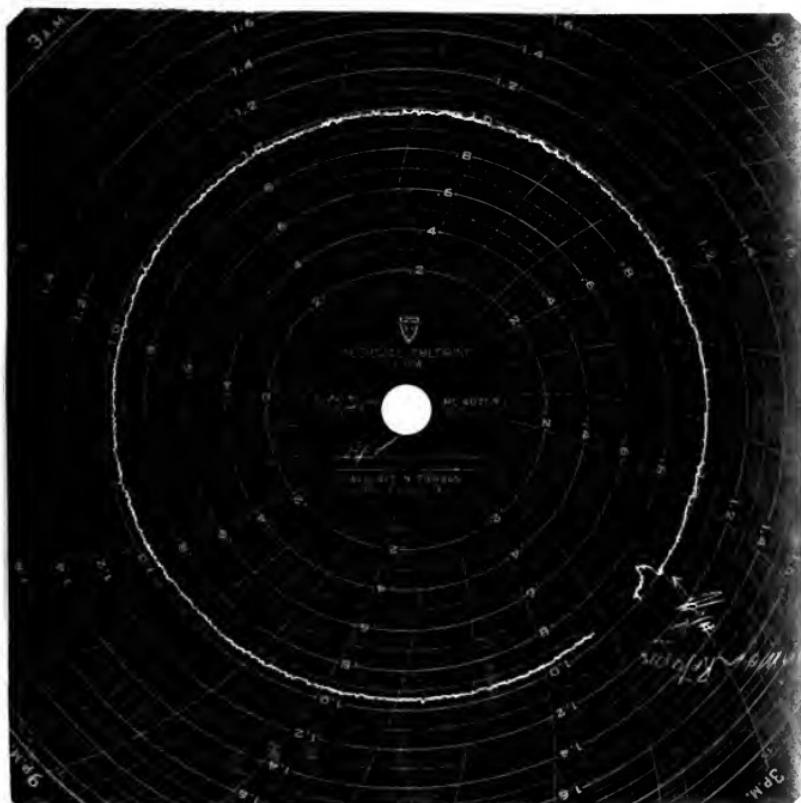


Fig. 21 - Typical Daily Chart from the Iodine Residual Recorder Which Monitors the Iodine Feed.



Fig. 22 - Typical Weekly Chart from the Iodine Residual Recorder Which Monitors the Iodine Feed.

a typical weekly chart, both from the instrument recording iodine feed, and Figure 23 shows a typical chart from the instrument recording iodine residuals in the distribution system. These analyzer-recorders are Wallace and Tiernan Series A-767 Amperometric Residual Recorders.\* These recorders are calibrated at two-week intervals with the Wallace and Tiernan Amperometric Titrator,\* which will be discussed in the laboratory study section. In addition to the continuous monitoring of iodine feed and distribution system residuals by these analyzer-recorders, other distribution system samples were taken and analyzed by amperometric titration and by means of an iodine test kit developed by Whittle.<sup>47</sup> This test kit will be described later. Table 9 presents typical iodine residuals at the ends of the distribution system for the indicated iodine dosages. This table shows that a substantial saving in iodine can be realized if only the necessary dose for adequate bacteriology is maintained.

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\* Products of Wallace and Tiernan, Belleville, New Jersey.



Fig. 23 - Typical Distribution System Weekly Chart from Iodine Residual Recorder. The Iodine Feed at this Time was 0.40 Parts Per Million.

Table 9

Iodine Residuals at Ends of the Two Water Systems for  
Indicated Iodine Dosages

Iodine Fed ppm	Range of Values for $I_2$ Residuals	Average Residual ppm	System Demand ppm
<u>Larger system serving women and girls</u>			
1.00	0.40 - 0.60	0.55	0.45
0.80	0.40 - 0.55	0.50	0.30
0.60	0.38 - 0.43	0.40	0.20
0.40	0.28 - 0.33	0.30	0.10
0.30	0.13 - 0.19	0.17	0.13
<u>Smaller system serving men's prison</u>			
1.00	0.60 - 0.80	0.75	0.25

Iodine Feed at Lowell

Disinfection of water with elemental iodine was begun in the system serving the Florida Correctional Institution for Women and the Forest Hill School for Girls at 2:30 PM on October 28, 1963, using an initial dosage of 1.0 parts per million of elemental iodine. On July 1, 1964, after eight months at this dosage level, it was supplemented by the addition of potassium iodide equivalent to 4.0 parts per million of iodide ion, to comprise a total dosage of 5.0 parts per million of elemental iodine plus iodide ion. The iodide was fed by means of hypochlorinators. This was continued for 64 days following which the feed of KI was discontinued. Feeding of elemental iodine was continued at the level of 1.0 parts per million until September 16, 1964, at which time a planned program of gradual reduction in dosage was begun. This gradual reduction was continued in step-wise fashion to  $0.30 \pm 0.05$  parts per million. This reduction in feed was carried out to determine the lowest iodine dosage for adequate bacteriology. The bacteriological results from this reduction in dosage will be presented later. The reason for the addition of the iodide was to see what effect, if any, this increased intake of the element would have on the human body. These physiological results will be described later.

Iodination was begun in the system serving the Florida Correctional Institution (Male Unit) at 9:00 PM on November 18, 1963, using the same dosage of 1.0 parts per million of elemental iodine. On July 3, 1964, this dosage was supplemented with 4.0 parts per million iodide as potassium iodide. After two months at this dosage, iodide feed was

discontinued and a dosage of 1.0 parts per million elemental iodine has been fed continuously since that time.

The dosages of iodine fed from October, 1963 through June, 1965 are shown in Figure 24.

#### Bacteriological Control

At the beginning of the study a routine sampling program was initiated which involved collecting samples for bacteriological analysis from all three wells and all three distribution systems twice each week. Ten samples were collected by the author each week for bacteriological analysis at the Earle B. Phelps Sanitary Engineering Research Laboratory of the University of Florida. Another set of ten samples was collected each week by the Marion County Health Department. Initially, these samples were shipped to Jacksonville and analyzed by the Florida State Board of Health. With the completion of a new bacteriological laboratory in the Marion County Health Department, located only seven miles from the institutions, collection and analysis of these samples was taken over by that laboratory. They determined the most probable number of organisms of the coliform group by the membrane filter technique and reported the non-coliform organisms as heavy, medium or light. The Earle B. Phelps Sanitary Engineering Research Laboratory determined the most probable number of organisms of the coliform group by both multiple tube and membrane filter techniques and, in addition, 24 hour standard plate counts at 35° C on all samples.

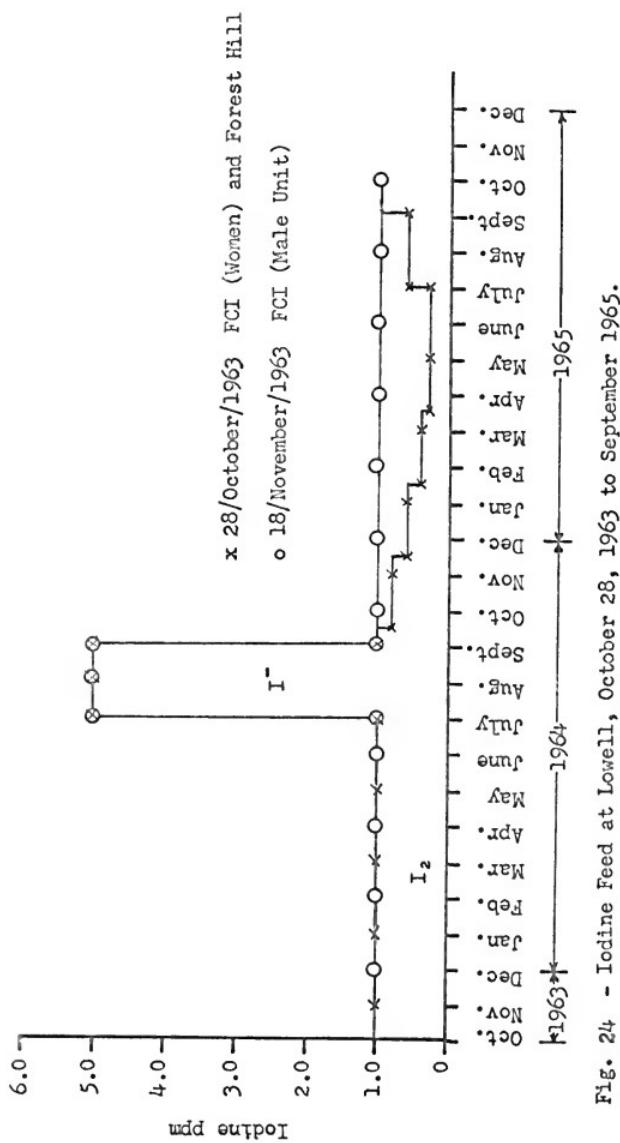


Fig. 24 - Iodine Feed at Lowell, October 28, 1963 to September 1965.

Bacteriology During the Chlorination Period

As has been stated earlier, water from two of the three wells used in this study frequently indicated the presence of coliform organisms, Well No. 1 30% of the time and Well No. 2 more than 50% of the time. Figures 25 and 26 show the results of the bacteriological examination of ten weekly samples by the Florida State Board of Health during the eight month period when calcium hypochlorite was employed. As expected, results obtained with the membrane filter technique show a lower percentage of unsatisfactory samples than results obtained by the multiple tube technique. On the basis of the data shown in Figure 25, water in the distribution systems met the criteria of the 1962 DRINKING WATER STANDARDS.<sup>46</sup> Figure 26 presents the data for non-coliform organisms during the same period. The samples from the system served by Station No. 1 had heavy growths of non-coliform organisms about 15% of the time, while the samples from the system served by Station No. 2 had heavy growths of non-coliform organisms about 10% of the time.

Figure 27 presents the data for coliform organisms for the same chlorination period obtained by the Earle B. Phelps Sanitary Engineering Research Laboratory by the multiple tube technique. On the basis of these data, only the water in the system served by Station No. 2 met the 1962 DRINKING WATER STANDARDS,<sup>46</sup> but water from Well No. 3, which supplies this system, meets these criteria without disinfection.

Figure 28 presents the data for the standard plate counts per milliliter at 35°C during the chlorination period in the distribution

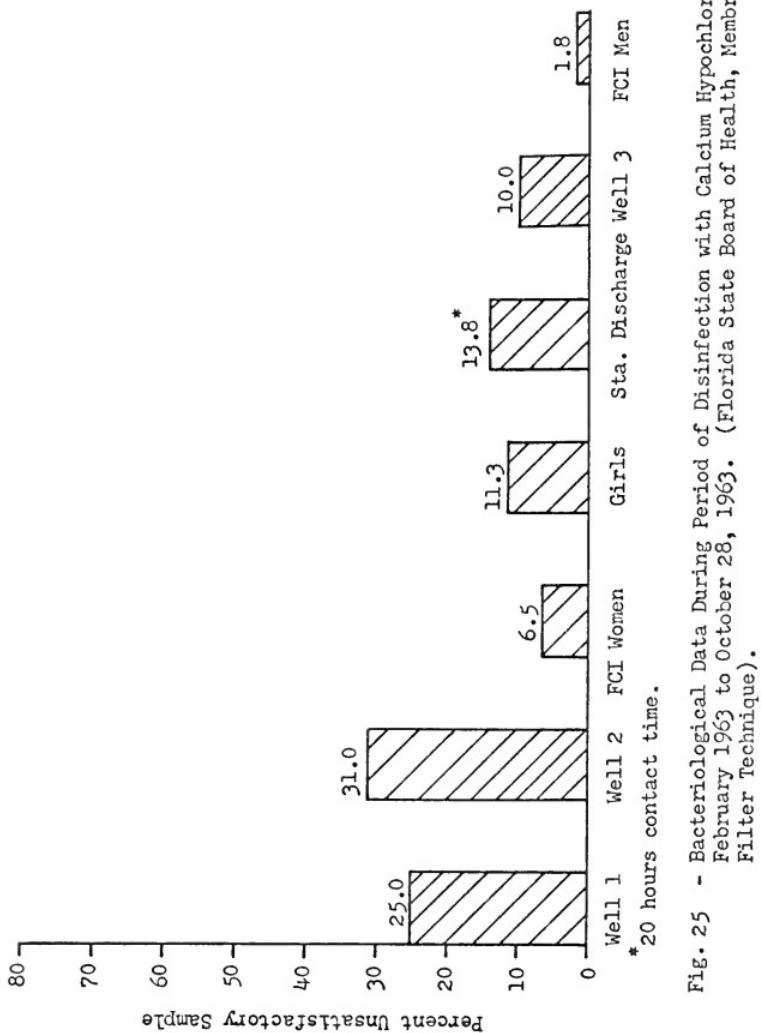


FIG. 25 - Bacteriological Data During Period of Disinfection with Calcium Hypochlorite, February 1963 to October 28, 1963. (Florida State Board of Health, Membrane Filter Technique).

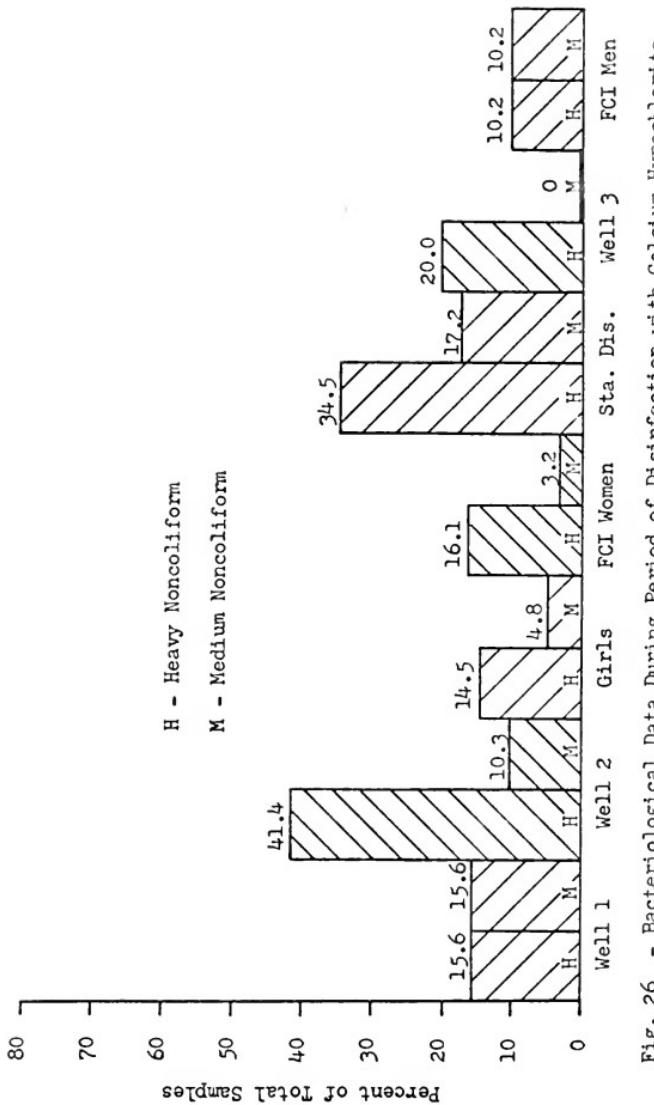


Fig. 26 - Bacteriological Data During Period of Disinfection with Calcium Hypochlorite, February 1963 to October 1963. (Florida State Board of Health, Membrane Filter Technique).

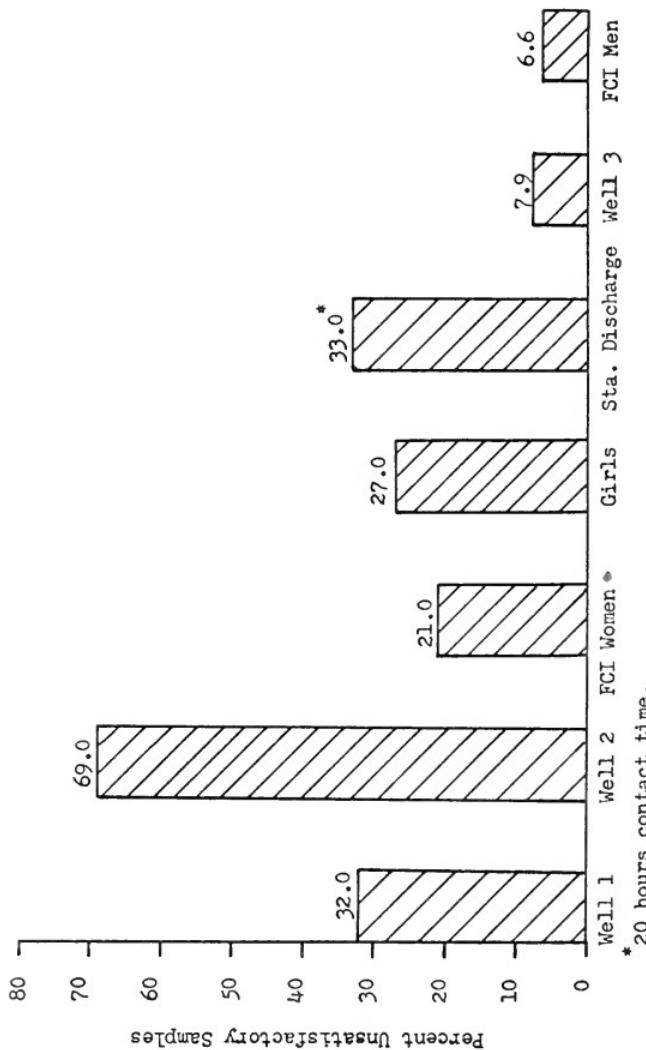


Fig. 27 - Bacteriological Data During Period of Disinfection with Calcium Hypochlorite, February 1963 to October 28, 1963. (Earle B. Phelps Sanitary Engineering Research Laboratory, Multiple Tube Technique).

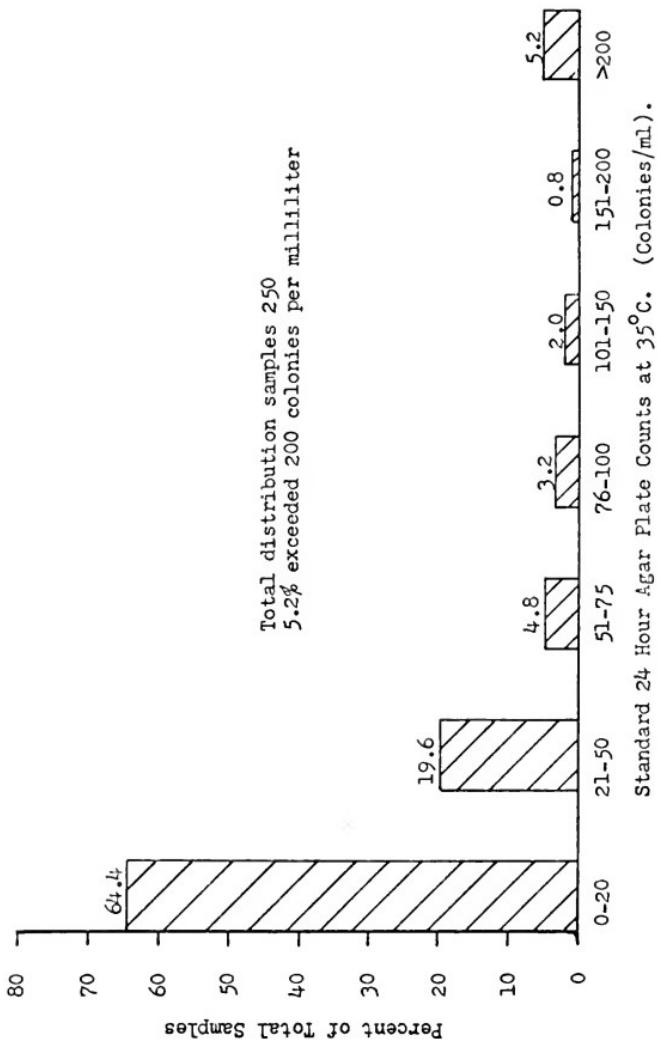


Fig. 28 - Bacteriological Data During Period of Disinfection with Calcium Hypochlorite, February 1963 to October 1963. (Earle B. Phelps Sanitary Engineering Research Laboratory).

systems. Of the 250 total samples, 64.6% were in the range 0-20 colonies per milliliter and 5.2% of the samples contained more than 200 colonies per milliliter.

It should be emphasized at this point that throughout the chlorination phase of this study, the water systems were still under operational control of the respective institutional staffs even though iodination equipment was being installed. The operators of both systems were not adequately trained and did not always have sufficient chlorine in the systems. This is apparent from the bacteriology and from the chlorine residuals found in the system by the author. Table 10 presents some of these data. Many times there were only trace quantities of chlorine or none at all in both systems. At other times there was as much as 2.0 parts per million free chlorine in the system. The operators did not determine chlorine residuals, but simply added a gallon of the hypochlorite solution to the solution tank of the hypochlorinator and fed the mixture. At times it would pump dry and at other times the discharge lines or suction lines for the pumps were clogged and no chlorine was being pumped. Frequently, much of the chlorine had volatilized from the stock solution before it could be used. The disinfection procedure as practiced here was less than adequate.

#### Bacteriology During Twenty-Two Months of Iodination

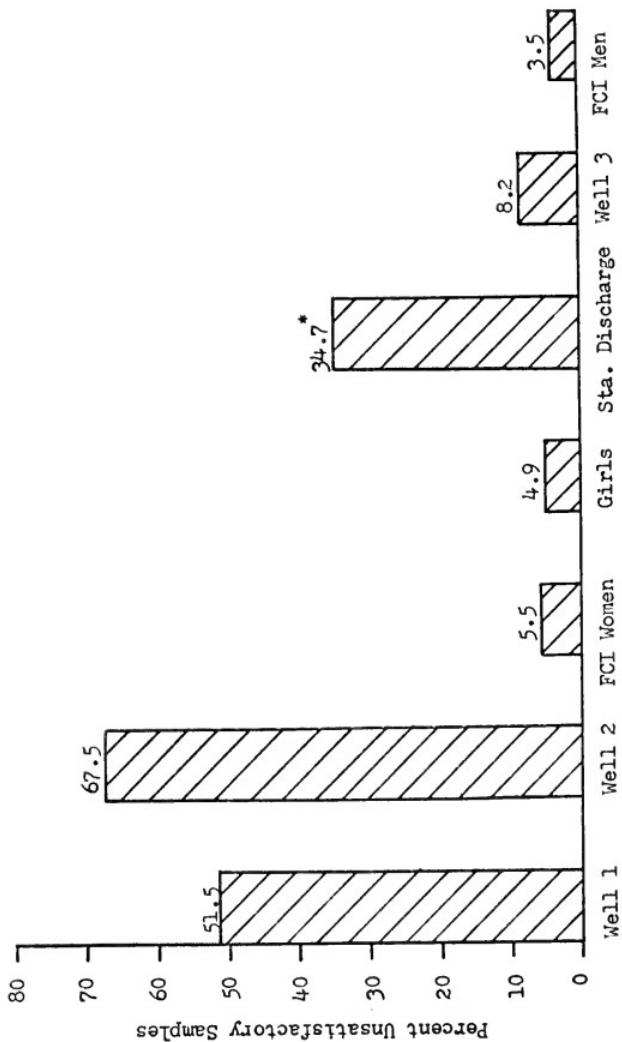
Iodination was begun on October 28, 1963, and Figures 29 and 30 present graphical analyses of bacteriological data obtained by the Florida State Board of Health during the 22 month period which has elapsed. Figure 29 presents the data for organisms of the coliform

Table 10

Typical Free Chlorine Residuals in Parts Per Million  
in the Distribution Systems Prior to Iodination

Girls School		Women's Prison				Men's Prison		
0.05	.05	0	0	0.05	0.10	0	0	0.10
0	.05	0	0.05	0.05	0.14	0	0.05	0.15
0	.05	0	0.05	0.05	0.10	0.05	0.05	0.15
0	.05	0.15	0.05	0.05	0.15	0.05	0.05	0.10
0.05	.05	0.18	0.05	0.05	1.50	0.05	0.05	0.10
0	.05	0.18	0.05	0.05	1.50	0.05	0.05	0.15
0	.05	0.10	0.05	0.05	0	0.05	0.05	0.10
0	.05	0.10	0.05	0	0.05	0.05	0	0.30
0	.05	0.10	0.05	0	0.25	0.05	0	0.20
0	.05	0.05	0.05	0	0.13	0.05	0	0.20
0.05	.05	0.10	0.05	0	0.05	0.05	0	0.30
0.05	.05	0.10	0.05	0.10	0	0.05	0.05	0.10
1.0	.05	0.14	0.05	0.10	0.25	0.05	0.05	0.15
.05	0	2.0	0.05	0.10	0.30	0.05	0.10	0.10

\* Each value represents a different day during an overall period of approximately eight months. Samples were collected at different points in the distribution system.



\* Two seconds contact time.

Fig. 29 - Bacteriological Data During 22 Months of Iodination, October 28, 1963 to September, 1965. (Florida State Board of Health, Membrane Filter Technique).

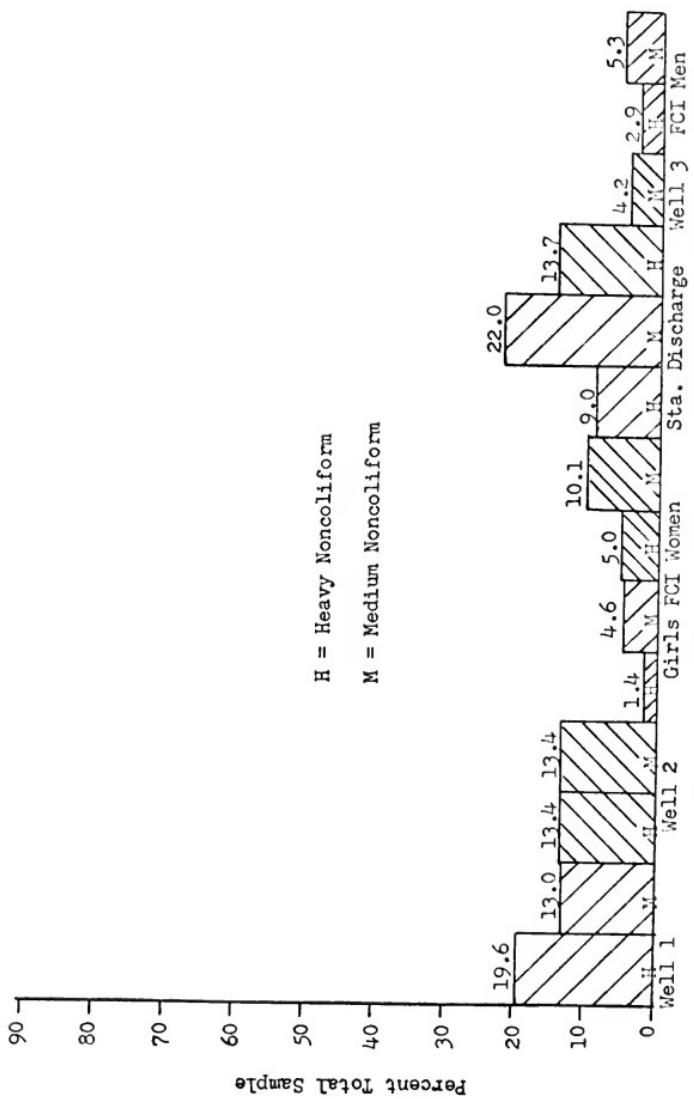


Fig. 30 - Bacteriological Data During 22 Months of Iodination, October 28, 1963 to September, 1965. (Florida State Board of Health, Membrane Filter Technique).

group. These data show a dramatic decrease in the number of unsatisfactory samples after disinfection with iodine. Percentages of unsatisfactory samples of 51.5% and 67.5% for Wells No. 1 and No. 2 respectively, drop to 5.5% for the Women's system and 4.9% for the Girl's system. The 8.2% unsatisfactory samples from Well No. 3 is reduced to 3.5% in the system. Figure 30 presents the non-coliform data for the iodination period. These data show a marked decrease in the number of non-coliform organisms after iodination. These data, accumulated by the Florida State Board of Health and totaling 544 samples, show that the water in the distribution systems far exceeds the criteria of the 1962 DRINKING WATER STANDARDS.<sup>46</sup>

Figure 31 presents the data using multiple tube techniques for coliform organisms from 787 samples, obtained by the Earle B. Phelps Sanitary Engineering Research Laboratory. The percentages of unsatisfactory samples from Wells No. 1 and No. 2, 37.5% and 67.1% respectively, were drastically reduced to zero in the Women's prison and to 1% in the Girl's school. Well No. 3 had 8.3% unsatisfactory samples, which was reduced to 0.6% in the distribution system of the male unit. These are substantial reductions and demonstrate the remarkable effectiveness of iodine in routine water disinfection. Standard plate count data are shown in Figure 32 for these same distribution system samples. About 80% are in the range 0-20 colonies per milliliter and 90.0% are below 50 colonies per milliliter. Only 2.9% of the 560 total distribution samples had plate counts above 200 colonies per milliliter. These data further substantiate the effectiveness of iodine as a water disinfectant.

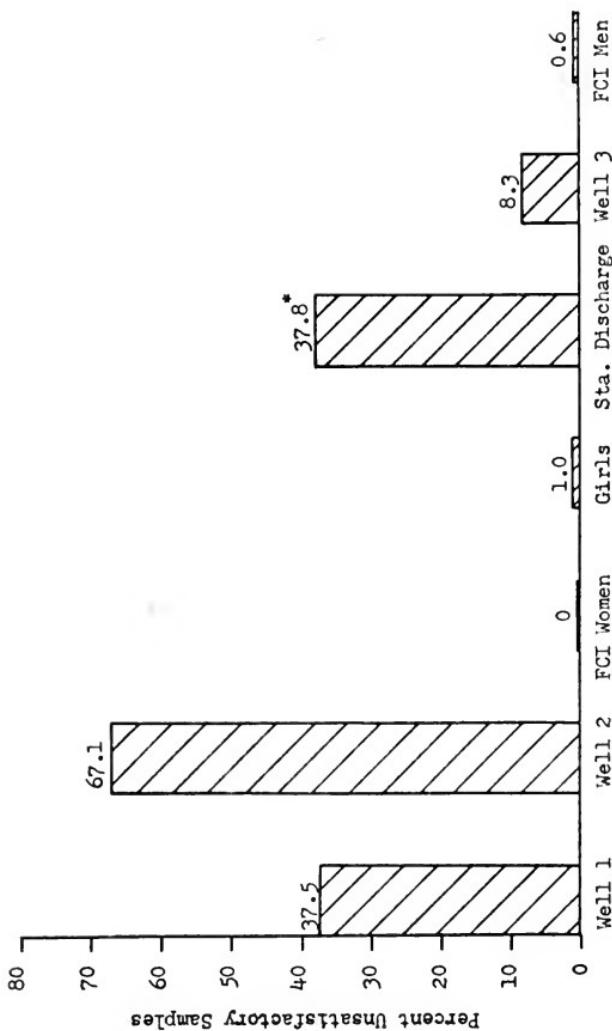


FIG. 31 - Bacteriological Data During 22 Months of Iodination, October 28, 1963 to September 1965. (Earle B. Phelps Sanitary Engineering Research Laboratory, Multiple Tube Technique).

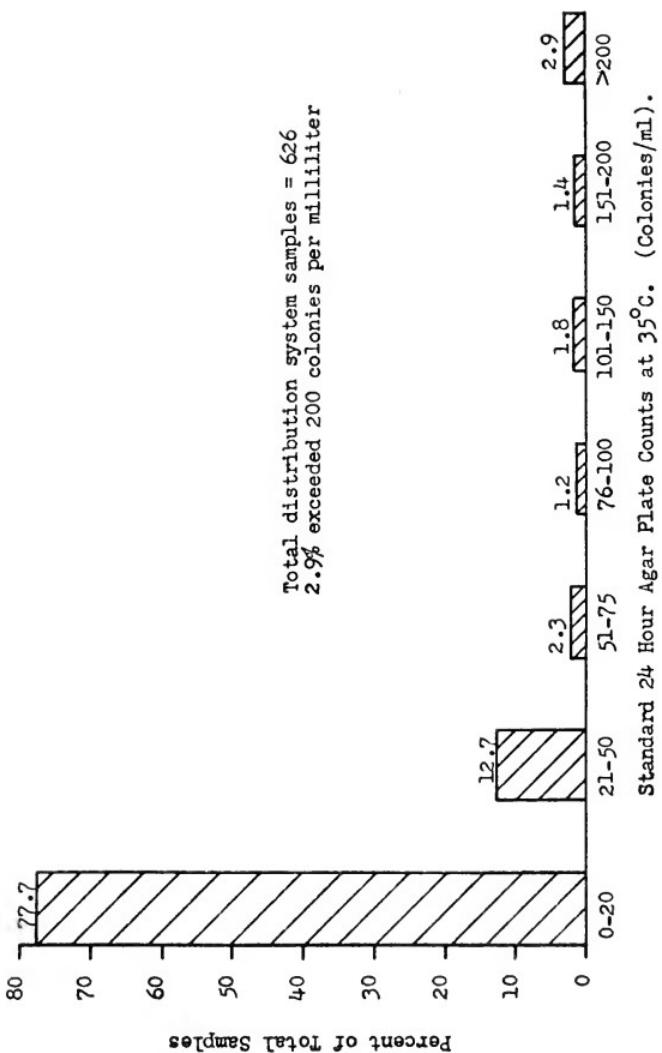


Fig. 32 - Bacteriological Data During 22 Months of Iodination, October 28, 1963 to September 1965. (Earle B. Phelps Sanitary Engineering Research Laboratory).

The iodine dosage was  $0.30 \pm 0.05$  parts per million during the collection of 72 of these 560 samples, hence, even this low dosage of elemental iodine proved to be highly effective.

The group of samples designated "station discharge" requires a word of explanation. Iodine solution was added to the water in the discharge header inside the pump station and these samples were collected just outside the station from the discharge line carrying iodinated water to the elevated tank. The contact time of the iodine with the water before its removal by the thiosulfate in the sample bottle was less than two seconds. In spite of this momentary contact time, the data in Figures 29 and 31 show that it was sufficient to reduce the number of unsatisfactory samples from Well No. 2 by about 50%.

#### Special Distribution System Bacteriological Study

This reduction in bacteria after only a brief contact time of two seconds was intriguing. Three experiments were run at the station discharge to study the effect of the short contact time of the iodine with the water on bacterial kill. Tables 11, 12, and 13 present these data. In all three experiments, after 15 seconds contact time of the iodine with water, there was considerable reduction in the MPN values and the standard plate counts. In two of the experiments the coliform density was reduced to satisfactory levels after only 45 seconds, and after one minute the coliform densities were reduced to satisfactory levels in all samples. These data represent actual distribution system conditions at the station discharge at Station No. 1 at Lowell.

Table 11

Typical Study Showing the Effect of Contact Time on  
Bacterial Kill, May 3, 1965

I <sub>2</sub> = 0.30 ppm		Temperature = 22.5° C		pH = 7.4
Contact Time	MPN/100 ml Multiple tube	MPN/100 ml Membrane filter	Standard 24 hour Plate Count at 35° C	
2 seconds	13	5	28	
15 seconds	2	<1	9	
30 seconds	5	<1	14	
45 seconds	2	<1	14	
1 minute	<2	<1	5	
5 minutes	<2	<1	8	
10 minutes	<2	<1	8	
15 minutes	<2	<1	10	
20 minutes	<2	<1	5	
25 minutes	<2	<1	9	
30 minutes	<2	<1	11	

Table 12

Typical Study Showing the Effect of Contact Time on  
Bacterial Kill, May 10, 1965

		$I_2 = 0.30 \text{ ppm}$	Temperature = $22.5^\circ\text{C}$	pH = 7.4
Contact Time		MPN/100 ml Multiple Tube	MPN/100 ml Membrane Filter	Standard 24 hour Plate Count at $35^\circ\text{C}$
2 seconds		49.	1	21
15 seconds		< 2.0	< 1	22
30 seconds		< 2.0	< 1	7
45 seconds		< 2.0	< 1	9
1 minute		< 2.0	< 1	7
5 minutes		< 2.0	< 1	13
10 minutes		< 2.0	< 1	10
15 minutes		< 2.0	< 1	7
20 minutes		< 2.0	< 1	13
25 minutes		< 2.0	< 1	13
30 minutes		< 2.0	< 1	23

Table 13

Typical Study Showing the Effect of Contact Time on  
Bacterial Kill, May 17, 1965

$I_2 = 0.30 \text{ ppm}$		Temperature = $22.5^{\circ}\text{C}$		pH = 7.4
Contact Time	MPN/100 ml Multiple Tube	MPN/100 ml Membrane Filter	Standard 24 hour Plate Count at $35^{\circ}\text{C}$	
2 seconds	49	26		47
15 seconds	22	1		9
30 seconds	8	< 1		11
45 seconds	< 2.0	< 1		11
1 minute	< 2.0	< 1		14
5 minutes	< 2.0	< 1		10
10 minutes	< 2.0	< 1		5
15 minutes	< 2.0	< 1		20
20 minutes	< 2.0	< 1		13
25 minutes	< 2.0	< 1		11
30 minutes	< 2.0	< 1		11

Physiological Control

The medical aspects of this study were under the direction of Dr. W. C. Thomas, Jr., Professor of Medicine in the J. Hillis Miller Health Center, University of Florida. He was assisted by Dr. Gerhard Freund and Dr. E. D. Bird, both Assistant Professors in the Department of Medicine. The dosages of iodine used for disinfection and those in excess of the amount required for disinfection were agreed upon after consultation with Dr. Thomas and his staff.

Medical Assessment and Selection of the Sample Population

Each fifth inmate of the prison community was selected for careful evaluation as to the effect of the iodinated water supply on the health and thyroid function of exposed individuals. Prior to and during the period when ingesting iodinated water, these test subjects were examined for evidence of rash or change in size or consistency of the thyroid gland. Additional procedures consisted of serial hematocrit determinations, white blood cell and differential blood counts, and determinations of radioactive iodine uptake by the thyroid gland (RAI), protein bound iodine (PBI) and serum thyroxine ( $T_4$ ). The physical examinations and RAI determinations were made at the prison by Dr. Thomas and members of his staff, while the PBI and  $T_4$  determinations were performed by the Bio-Science Laboratories, Los Angeles, California.

Physiological Response to Iodine Intake

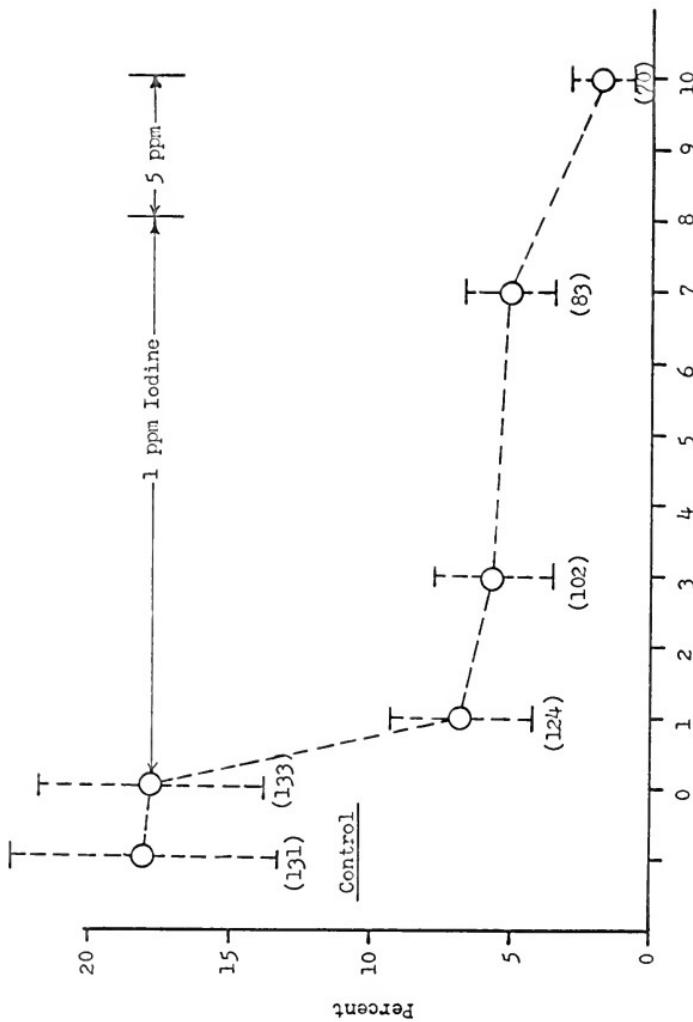
During the period of medical evaluation, discharge of some of the prisoners resulted in gradual attrition in the number of test subjects selected initially. One hundred and twenty-five inmates were

evaluated twice, and eight inmates only once, prior to iodination of the water supply. Seventy of the prisoners were available for examination during the entire study period. Although at the outset the test group was divided almost equally into adult males, adult females and 13 to 16 year old Negro girls, losses from the group during the study were largely among the adult males and teen-age girls.

Figure 33 shows the effect of iodine ingestion on radioactive iodine uptake (RAI). Values plotted are the mean values for the group plus or minus one standard deviation. After 30 days use of iodinated water the mean value for RAI had decreased from about 17% to about 7%. Values determined at the end of three months and of seven months of feeding 1.0 parts per million of iodine showed little further change. However, increasing the dosage to a total of 5.0 parts per million iodine plus iodide for 60 days decreased the mean RAI to about 2%.

Figure 34, plotted on the same time scale, shows the changes in mean values for protein bound iodine (PBI) during the ten month period. There was a slight increase at the end of the first month of iodine feed, a further slight increase at the end of the third month, no further increase at the end of the seventh month, and a small but definite increase at the end of the tenth month following 60 days of feeding 5.0 parts per million of iodine plus iodide. It is to be noted, however, that until the iodide content of water was increased to 5.0 parts per million the mean PBI values were well within the normal range of 4-8  $\mu\text{g}/100 \text{ ml}$ .

Figure 35, plotted on the same time scale, shows clearly that



( ) Refers to number of observations.

Fig. 33 - Radioactive Iodine Uptake, Mean Values  $\pm$  One Standard Deviation.

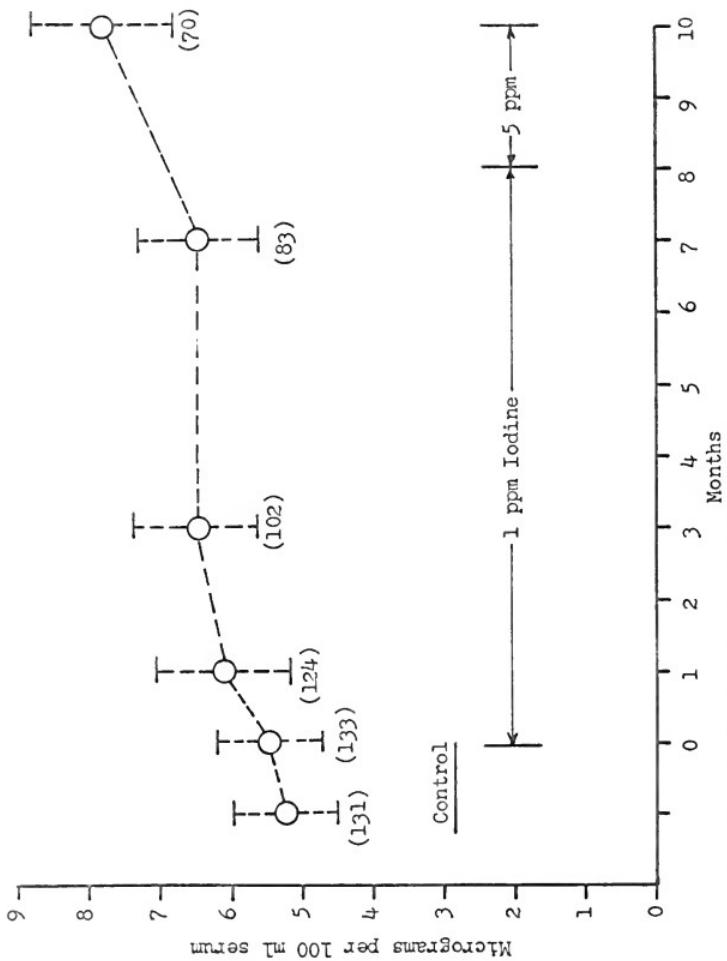
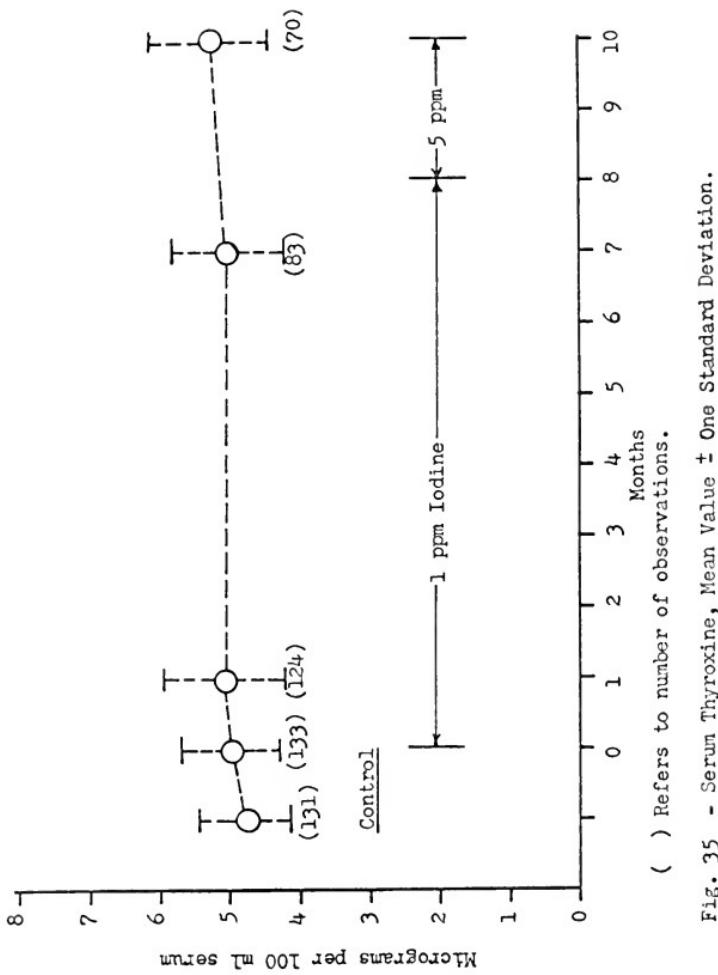


Fig. 34 - Protein Bound Iodine, Mean Value  $\pm$  One Standard Deviation.  
( ) Refers to number of observations.



( ) Refers to number of observations.  
Fig. 35 - Serum Thyroxine, Mean Value  $\pm$  One Standard Deviation.

there was no significant change in the mean values for the concentration of thyroxine in sera during the entire ten month test period.

A study of urinary iodide excretion was made later in the program when the iodine dosage had been reduced to 0.60 parts per million.

Figure 36 presents these data. It was found that the urinary iodide was more than 500 micrograms per gram of creatinine excreted in each of the 50 inmates studied, thus confirming the usefulness of this ratio in estimating iodine intake.

During the entire test period and during the many months of continuous iodination which have followed, there has been no evidence of allergic reactions to iodine or any change in the size of the thyroid gland. To date there is no evidence that iodine, under the experimental conditions employed, has had any detrimental effect on general health or thyroid function either when ingested in drinking water or, as will be shown later, on individuals exposed to swimming pool water disinfected with iodine.

#### Aesthetic Considerations

A number of interested scientists have visited the institutions and each has been requested to attempt to identify any tastes or odors which may be present in the water. These people represent eleven different foreign countries and thirteen different states of the United States. In addition, several test panels have been conducted using graduate students as highly qualified participants. These laboratory data will be presented in the laboratory studies section. The institutional personnel and inmates have volunteered comments from time to

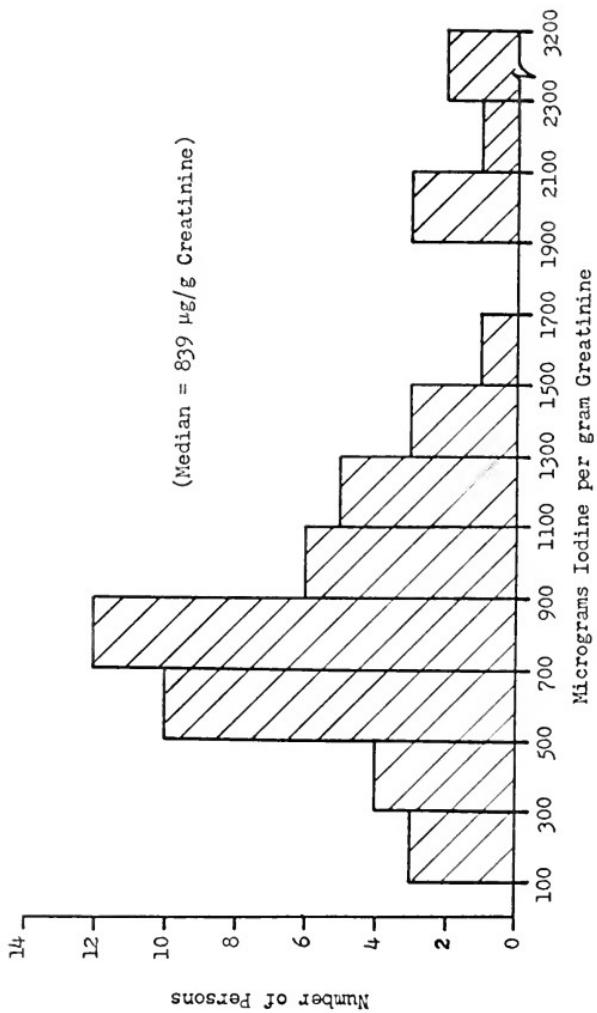


Fig. 36 - Urine Iodide in 50 Subjects Using Iodinated water which Contained 0.6 Parts Per Million Elemental Iodine.

time and these comments reveal the psychology of change and the subjectiveness of taste. Some have been very objective. A few have been based purely on superstition. It can be stated, based upon all of these observations, that few if any persons are able to detect a concentration of one part per million of elemental iodine in the water by either color, taste or odor. Iodide ion cannot be detected in concentrations far exceeding five parts per million. When the concentration of elemental iodine is 1.5 to 2.0 parts per million, many people will be able to detect a taste, but it will not be a definable taste identifying it as iodine, and it will not be an objectionable one. It may be described as faintly sweetish and not unpleasant. Elemental iodine begins to impart a color to water, which is detectable by experienced observers in a clear glass against a white background at concentrations from 2.0-2.5 ppm. Iodine, in water disinfection concentrations, combines very slightly, if at all, with many types of organic compounds so that the production of tastes and odors from this source is minimized. This point will be covered more fully in the laboratory studies which follow.

#### Public Acceptance at Lowell

At the beginning of this project, many guards and civilian employees were unhappy at the thought of iodine in their water supply. Most could only visualize iodine as tincture of iodine, a very poisonous compound found in the home medicine cabinet. None were able to detect exactly when we began iodination and there have been no real complaints during more than twenty-two months of iodination, even though many of the staff live at the institutions. This is substantial evidence that

there are no objectionable tastes and odors associated with routine water disinfection employing elemental iodine.

Disinfection of the Water of the University of Florida Swimming Pool with Iodine

Introductory Remarks

Iodine has been shown to be an effective swimming pool water disinfectant by many researchers,<sup>6,7,8,9</sup> and as a result has to date been approved for this purpose by eight states. The U. S. Public Health Service issued provisional approval of the use of iodine in December, 1962 as follows: "The Public Health Service believes that until more definitive information is available, iodine is an acceptable disinfectant for use in swimming pool waters provided the maximum concentration of iodine in all forms does not exceed five parts per million."<sup>36</sup> This study was initiated utilizing the 500,000 gallon Olympic-size outdoor pool of the University of Florida to investigate the physiological, bacteriological, and chemical aspects of a total iodine-iodide concentration of five parts per million in swimming pool water. The medical evaluations were carried out by Dr. W. C. Thomas, Jr. and members of his staff.

Swimming Pool Characteristics

The University of Florida swimming pool is one of the oldest and largest swimming pools in Florida. It was originally designed as a fill-and-draw pool and hence does not fit the modern concept of swimming pool design. The pool is 60 feet wide and 150 feet in length and varies in

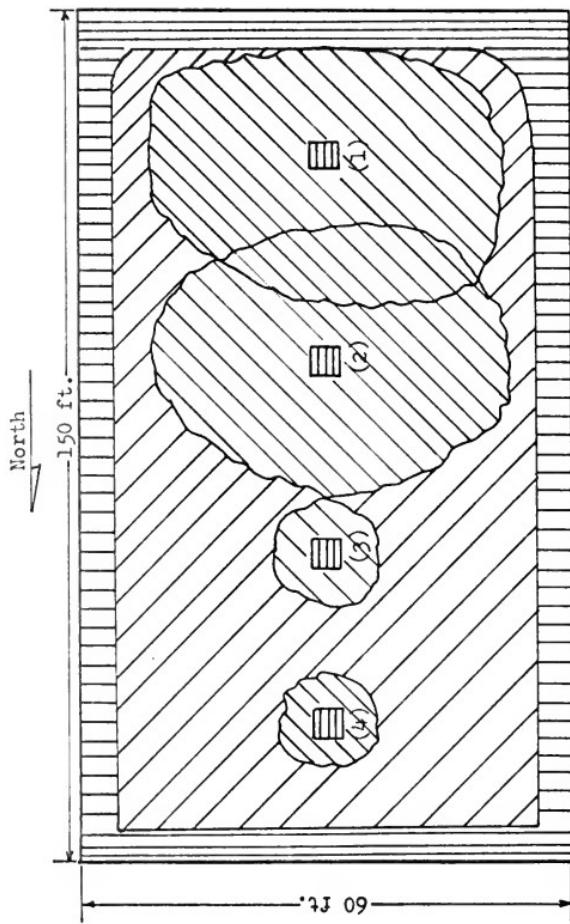
depth from four feet to 12 feet. Its surface area is 9000 square feet and it has a volume of 500,000 gallons.

At the time of this study the pool recirculation system was woefully inadequate.\* Figure 37 depicts the dead spaces in the pool where no recirculation takes place, except as the swimmers mix the water by their movements. The large volume of water in these areas was extremely difficult to disinfect, especially when there were few or no people swimming in the pool.

The water left the pool by means of the scum gutter around the periphery of the pool and was returned to one of two sumps. These sumps were interconnected and the recirculation pump suction line extended into the east sump. The water was taken from this sump and pumped through one of three diatomite filters. After leaving the filters, the water received the disinfectant just before it reached the pool. Chlorine gas was the disinfectant used prior to this study. The filter discharge line had only four openings into the pool spaced along the center line at the bottom of the pool. Most of the recycled water entered the pool through two of these four openings in the deep end. At the pumping rate of 1100 gallons per minute, there was a theoretical turnover of water every 7.5 hours, but due to the very poor circulation much of this recycled water was probably the same water, and hence the actual time for a complete turnover was much greater than eight hours.

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\* As a result of this study, \$33,000 was appropriated to renovate the pool recirculation system, and purchase new diatomite filters. This task has been completed, and the pool modernized.



( ) Refers to numbered inlets to pool.

Almost no recirculation 100% of the time. Recirculation depends on bathers mixing the water and thermal gradients.

Partial recirculation while pool is in use. Bathers determine the amount of recirculation.

Adequate recirculation. 90% of the water comes from inlets (1) and (2).

Fig. 37 - Pool Recirculation Pattern, Summer of 1964.

This extremely poor recirculation made it difficult to achieve adequate disinfection, because of the many dead spots along the side walls and the bottom of the pool. Two one-quarter inch thick steel plates were fabricated and placed over the two inlets supplying most of the water to the pool, in order to partially block these openings and hence get more water from the other two inlets at the shallow end of the pool. This procedure helped considerably, but the pool still required constant attention and special handling in order to meet recommended sanitation standards for swimming pools.

Disinfection System

Disinfection was accomplished by a gaseous chlorinator prior to this study. This chlorinator had a rated capacity of from 0-100 pounds of chlorine per 24 hours and was not operating at full rated capacity when the first bacteriological samples were taken, and hence the pool was unsanitary. This is a typical situation in chlorine disinfected swimming pools, resulting from the improper use of the orthotolidine reaction with chlorine. Even though the chlorinator was not functioning properly and the quantity of chlorine reaching the pool was insufficient, the pool operator would use his test kit and read 0.3 or 0.4 parts per million "free" chlorine and feel very secure in the belief that the pool was in a sanitary condition. The Rules of the Florida State Board of Health<sup>48</sup> Chapter 1700-3, section 14 require: "Chlorine disinfection shall be provided on all pools and the residual in any part of the pool shall be maintained at a minimum concentration of 0.3 parts per million at all times." What this operator failed to consider,

and this occurs at the majority of chlorine disinfected swimming pools, is that combined available chlorine reacts with the orthotolidine reagent at the temperature of the pool water. The temperature may be near 30°C in Florida, and at this temperature a combined chlorine residual reacts as if it were free chlorine. Combined available chlorine is only one twenty-fifth as effective as free available chlorine,<sup>44</sup> and hence 0.3 parts permillion combined available chlorine is not sufficient to maintain a sanitary swimming pool. The bacteriological data for this pool for the period prior to iodination dramatically illustrate how chlorine-disinfected pools may be quite unsanitary even though the operator is taking samples regularly and determining chlorine residuals. In order to determine free chlorine residuals by the orthotolidine procedures in the presence of combined available chlorine residuals, the sample must be chilled to 1°C. Free chlorine reacts almost instantaneously, even at 0°C, whereas combined available chlorine reacts much slower at the low temperatures. These procedures and precautions are carefully spelled out in STANDARD METHODS,<sup>49</sup> but they have not been sufficiently explained to most swimming pool operators and certainly not understood and practiced by them.

Water Analysis

Table 14 presents the results of a chemical analysis of the pool water for June 26, 1964.

Table 14

Chemical Analysis of the University of Florida  
Swimming Pool Water

Constituent	Concentration (parts per million)
Total Dissolved Solids	164
Silica, $\text{SiO}_2$	3.4
Iron, $\text{Fe}^{+++}$	0.06
Calcium, $\text{Ca}^{++}$	28.
Magnesium, $\text{Mg}^{++}$	10.
Sodium and Potassium as $\text{Na}^+$	8.7
Bicarbonate, $\text{HCO}_3^-$	29.
Sulfate, $\text{SO}_4^{=}$	35.
Chloride, $\text{Cl}^-$	48.
Iodide, $\text{I}^-$	4.9
Fluoride, $\text{F}^-$	0.63
Nitrate, $\text{NO}_3^-$	0.40
Carbonate Hardness as $\text{CaCO}_3$	35.
Non-carbonate Hardness as $\text{CaCO}_3$	76.
Total Hardness as $\text{CaCO}_3$	111.
pH 7.40	

Iodination Criteria and Procedure

Since one of the primary objectives of this study was to determine the physiological effects of 5.0 parts per million total iodine-iodide, the iodide concentration was maintained at between 4.5 parts per million and 5.5 parts per million by daily analysis and addition as required. The iodide was introduced into the pool in the form of potassium iodide after the chlorine residual was allowed to go to zero. An initial amount equivalent to 5.0 parts per million as iodide ion was spread uniformly throughout the pool. This required 28 pounds of potassium iodide. Iodine was released by adding initially a small amount of calcium hypochlorite and then after a period of four days, gaseous chlorine. The chlorine was fed intermittently as the iodine residual dropped below a minimum residual of 0.30 parts per million. A concentration range of from 0.30-0.60 ppm of iodine was maintained at a pH which varied from 7.3 to 7.6. Commercial grade muriatic acid was used to control pH. These values were maintained at the sides of the pool, but  $I_2$  residuals immediately above the inlets were considerably higher during the release period. All halogen residuals were measured with a Wallace and Tiernan amperometric titrator and pH values were determined with a Beckman Model G pH meter.\* The pool filters were backwashed once per day and the pool was vacuumed once per week. At the end of the iodination period, all remaining iodine and iodide was converted to iodate. This conversion was accomplished by adding a very large excess of strongly alkaline calcium hypochlorite (HTH) and raising the pH well above 8.0.

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\*A product of Beckman Instruments, Inc., Fullerton, California.

#### Chlorination Criteria and Procedure

At the conclusion of the iodination test the pool was put back on chlorine and supervised for one more week. Sufficient chlorine was fed to maintain a free residual of 0.3-0.6 ppm at a pH of 7.3 to 7.6. Both chlorine gas and calcium hypochlorite solution were required to maintain these residuals. Soda ash ( $\text{Na}_2\text{CO}_3$ ) was used to control pH. The chlorine residuals were determined by amperometric titration and the pH as before. Both chlorine and iodine in the range of 0.30 to 0.60 parts per million are effective germicides, as indicated by the bacteriological data obtained in this study.

#### Filtration

The pool recirculation system was operated continuously throughout the iodination and chlorination periods, with the exception of a daily filter backwash requiring about one hour and a weekly vacuum of the bottom requiring about five hours. Even with this 24 hour per day operation it is doubtful if the pool water was completely recycled during a 24 hour period. The poor recirculation of this pool resulted in only a partial turnover of the water.

#### The Weather

Air temperatures were well above  $90^{\circ}\text{F}$  for all but four days of the entire test period. Those temperatures were in the high 80's. The temperature of the water stayed very near  $86^{\circ}\text{F}$  and on a few occasions the water temperature rose to  $88^{\circ}\text{F}$ . See Table 15.

On seven days of the iodination period there were brief but

Table 15  
Swimming Pool Data During Iodination

Date	Temperature °F		pH	Average Iodine Residuals (ppm)		
	Air	H <sub>2</sub> O		Morning	Noon	Evening
June 16	98	88	7.8	0	0.12	0.08
17	98	88	7.8	0.03	0.25	0.05
18	98	88	7.8	0.58	0.12	0.18
19	96	88	7.7	0.51	0.11	0.45
20	96	88	7.7	0.07	0.61	0.41
21	93	88	7.7	0.98	0.43	0.19
22	95	88	7.7	0.45	0.45	0.24
23	94	88	7.6	0.59	0.32	0.31
24	95	88	7.6	0.56	0.24	0.29
25	92	88	7.6	0.37	0.24	0.21
26	92	88	7.5	0.69	0.78	0.36
27	88	86	7.5	0.63	0.35	0.34
28	91	87	7.6	0.35	0.13	0.13
29	91	86	7.5	0.56	0.22	0.46
30	89	86	7.5	1.10	0.51	0.33
July 1	90	86	7.6	0.85	0.44	0.39
2	86	86	7.4	0.83	0.27	0.43
3	89	86	7.6	1.50	1.04	0.49
4	91	87	7.5	1.53	0.83	0.28
5	92	88	7.5	0.75	0.38	0.15
6	91	88	7.3	0.73	0.37	0.35
7	91	88	7.6	1.08	0.33	0.33
8	92	88	7.6	0.70	0.35	0.34
9	93	88	7.5	0.80	0.33	0.35
10	90	86	7.6	1.10	0.45	0.31

heavy showers. These resulted in from 0.10 inches of rain up to 1.10 inches of rain. Usually these showers were accompanied by high winds, which blew considerable debris into the pool. Swimmers were ordered out of the pool during these severe weather periods, which usually lasted only a few minutes.

Pool Bathing Load

The bathing load during the iodination period was fairly heavy. There were swimming classes each weekday plus the recreational swimming. Table 16 shows that the lowest number of bathers for any one day was 85 and the highest number for any one day was 372. The average daily bather load was 236. This load consisted of about 50% men and 50% women, all of whom were of college age or above. Most of these people were in the 18 to 25 year age bracket, but there were some in their forties (44, 49, etc.).

Table 17 shows the swimming pool bathing loads during the one week of supervised chlorination. The bathing loads during this period did not differ appreciably from the bathing loads during the iodination period. The average bathing load was 243 versus an average bathing load of 236 for the iodination period.

Table 16  
Pool Bathing Loads During Iodination

Date	Number of Bathers	Date	Number of Bathers	Date	Number of Bathers
June 16	259	June 25	321	July 4	113
17	334	26	158	5	182
18	343	27	123	6	223
19	193	28	149	7	322
20	146	29	204	8	286
21	178	30	299	9	342
22	332	July 1	259	10	85
23	372	2	223		
24	312	3	148		

Average bathing load - 236

Table 17  
Pool Bathing Loads During One Week of Supervised Chlorination

Date	Number of Loads
July 13	243
14	405
15	254
16	281
17	30

Average bathing load - 243

Sampling Procedures

Chemical Samples - Samples for halogen determination were collected in 600 milliliter plastic beakers at arms length under the water surface at the shallow end, the middle and the deep end of the pool at least once per hour during pool operation. These samples were collected and analyzed immediately at the pool.

Bacteriological Samples - These samples were taken from the periphery of the shallow half of the pool. They were collected in a two-liter bottle fastened to a long stainless steel tube. This bottle was kept full of strong HTH solution between sampling periods. The bottle was emptied of HTH solution, rinsed three times by filling with pool water, and then the sample was collected by pulling the bottle through the water along each side of the shallow half of the pool. The bottle was started at a depth near the bottom and raised slowly as the end of the sample cycle was approached. This allowed a representative sample, taken from the bottom to the top of the pool and from the middle of the pool to the end of the shallow half of the pool. This same bottom-to-top procedure was followed along the shallow end of the pool also. After the sampling bottle was removed from the water, a portion of the sample was wasted and then the actual sample was poured into the sterilized sample bottle, which contained sodium thiosulfate to neutralize any halogen present in the sample. The samples were taken immediately to the bacteriological laboratory for analysis within minutes of the collection time. The Earle B. Phelps Sanitary Engineering Laboratory is about one block from the pool. This method of sampling provides more

representative samples than a mere grab sample taken at arms length from the side of the pool. The pool was sampled three times daily on each weekday at morning, noon, and late afternoon. All of these samples were taken in the shallow half of the pool, where circulation was extremely bad. These data are found in Table 18.

Table 18

Swimming Pool Data During One Week of Supervised Chlorination

Date	Temperature °F		pH	Free Chlorine Residuals (ppm)		
	Air	H <sub>2</sub> O		Morning	Noon	Evening
July 13	90	84	7.6	0.46	0.02	0.04
14	94	86	7.2	0.27	0.18	0.53
15	95	86	7.4	0.65	0.57	0.54
16	89	86	7.5	0.30	0.27	0.29
17	88	84	7.6	0.26	0.33	1.04

Bacteriological Results

Both iodine and chlorine were shown to be effective disinfecting agents in the concentration range 0.3 to 0.6 mg/l at a pH from 7.3 to 7.6. Figures 38 and 39 graphically show this. Of the 162 samples checked for coliform bacteria during the iodination period, 95.7% or 155 of them were found to be free of coliforms. Of these same samples, 94.5% or 153 were free of Enterococcus. Some of the bad samples were collected during thunder showers, which may have contributed to their

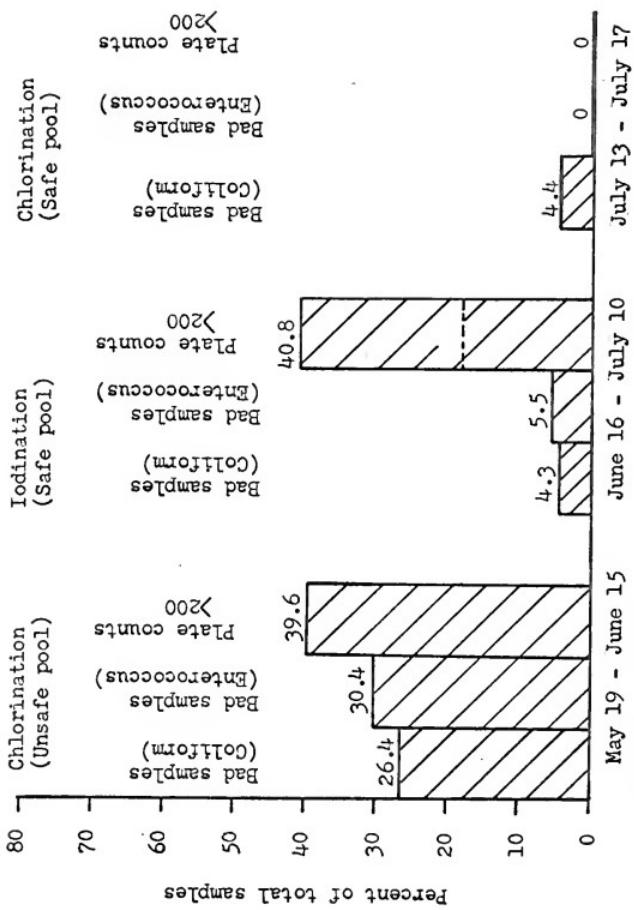


Fig. 38 - Bacteriological Data During Iodination of the University of Florida Swimming Pool, May 19 to July 17, 1964. (Earle B. Phelps Sanitary Engineering Research Laboratory).

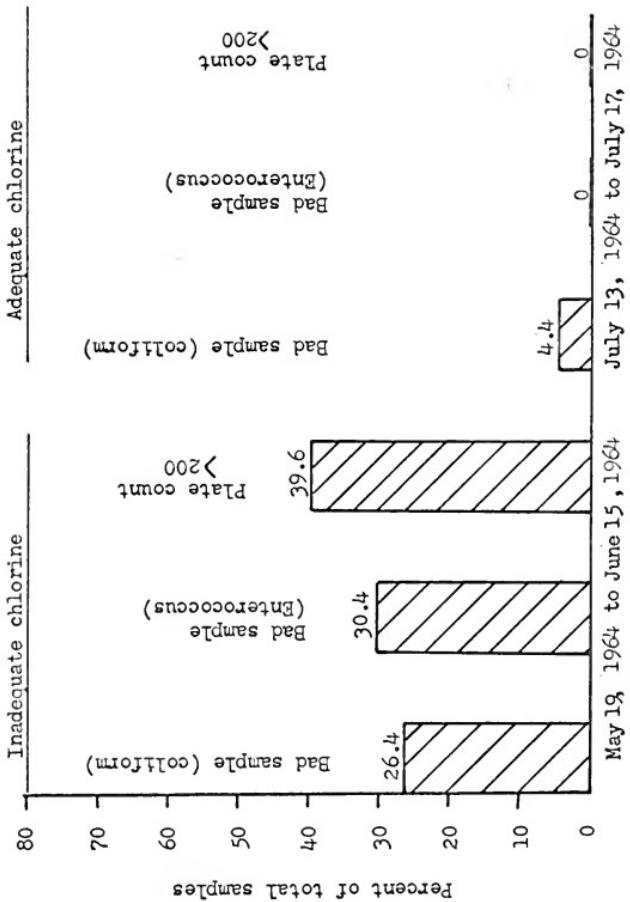


Fig. 39 - Bacteriological Data During Chlorination of University of Florida Swimming Pool. (Earle B. Phelps Sanitary Engineering Research Laboratory).

contamination. More than half of the standard plate counts were below 200 (59.2% of 159 samples were less than 200) during the iodination period. In addition, 22.7% of those > 200 were collected during the first four days. These results are far better than are required by the U. S. Public Health Service swimming pool standards.

Chlorine provided satisfactory disinfection although it was difficult to achieve and very hard on the swimmers' eyes. The chlorine disinfection period of the test lasted for only one week, but the results are significant. Only 4.4% of the 45 total samples contained coliforms and none of the 45 contained any Enterococcus. All of the 45 samples had a standard plate count less than 200. The chlorine residuals were very difficult to maintain in comparison with the iodine residuals. All of the bacteriological tests were run in conformance with the 11th Edition of Standard Methods for the Examination of Water and Waste Water.

Table 19

Bacteriological Data for Period May 19 - June 15  
(Prior to Iodination)

	Coliform	Enterococcus	SPC
Total Samples	174	174	174
Bad Samples	46	53	
Good Samples	128	121	
SPC >200			69
% Bad *	26.4	30.4	
% Good	73.6	69.6	
% SPC >200			39.6

Not one day without bad samples. Chlorine residuals inadequate and sometimes nonexistent.

\* PHS Drinking Water Standards permit a maximum of 15% bad samples.

Table 20  
Summary of Bacteriological Data, June 16 - July 17

	Iodine			Chlorine		
	Coliform	Enterococcus	SPC	Coliform	Enterococcus	SPC
Total Samples	162	162	159	45	45	45
Bad Samples	7	9	0	2	0	0
Good Samples	155	153		43	45	
SPC > 200			65			0
% Bad	4.3	5.5		4.4	0	
% Good	95.7	94.5		95.6	100	
% SPC > 200			40.8			0

Note: Two of the seven bad coliform samples taken during the period of iodine disinfection were taken on the first day when there was no residual halogen (either Cl<sub>2</sub> or I<sub>2</sub>) in the pool. Three of the nine bad enterococcus samples were taken during this same period when there was no residual halogen in the pool. Of the SPC's over 200, more than one-half of the 40.8% (22.7%) were taken during the first four days of the test period when operating conditions were transitory.

#### Algae Control

The pool contained numerous patches of brown algae at the beginning of the iodination period. This growth was along the red stripes marking the lanes of the pool on the bottom and up the wall of the north (shallow) end of the pool. The iodine did not remove this algae, but the algae did not spread. A very small amount of brown algae developed around the ladders. This was due to very poor circulation. The ladders are set back in a slot in the wall and can receive no circulation at all,

except when a swimmer stirs the water up as he leaves the pool by way of the ladder. This same growth was visible during the chlorination period. It was removed only when granular calcium hypochlorite (HTH) was rubbed directly against the algae on each of several days. This finally removed most of the brown algae. The paint seemed to have some bearing on the presence of the algae, since it grew only on the red stripes used for lane markers.

#### Physiological Control

It has long been known that iodine can be absorbed through the skin. When iodine tincture is painted on the body some of it is absorbed. Also, iodine has been absorbed through the skin during reactor incidents.<sup>50</sup> Since the Public Health Service has approved the use of five parts per million total iodine-iodide for swimming pool water disinfection, it was thought desirable to determine whether or not swimmers would absorb any of this iodine through the skin from the pool water. To investigate this possibility twenty-two swimmers were selected at random and each received a physical examination before and after swimming for one month in the iodinated pool. Determinations of RAI uptake, protein bound iodine (PBI) and serum thyroxine ( $T_4$ ) were made on these individuals before and after swimming in from 4.5 to 5.5 parts per million total iodine-iodide in the same manner in which they were made in the Lowell studies. Thyroid glands were examined for size and any unusual manifestations. Exposure time of the group as a whole was 240 hours, and the average exposure time per swimmer was 11 hours and 40

minutes. The shortest exposure time was 5 hours and 35 minutes, while the longest exposure time was 31 hours and 44 minutes. The average values for RAI, PBI, and  $T_4$  before and after exposure are shown in Table 21. Figures 40 and 41 illustrate the effect of swimming in iodinated water for three hours per week on the RAI and PBI. Careful study of these data reveals no significant change in any of the three indices of thyroid function. In addition, no evidence of allergy to iodine or change in size of the thyroid glands was detected in any subject during the study.

Table 21  
Medical Test Results of University Swimming Pool Study

PBI		$T_4$		RAI	
$\mu\text{g}/100 \text{ ml serum}$		$\mu\text{g}/100 \text{ ml serum}$		Percent	
Before	After	Before	After	Before	After
5.7 $\pm$ 0.75	5.7 $\pm$ 0.75	4.8 $\pm$ 0.69	4.9 $\pm$ 0.70	19.8 $\pm$ 4.50	18.1 $\pm$ 4.25
Normal 4.0 - 8.0		Normal 3.5 - 7.5		Normal 10.0 - 35.0	

Mean value  $\pm$  one standard deviation before and after swimming in the iodinated pool.

PBI = protein bound iodine in  $\mu\text{g}/100 \text{ ml serum}$ .

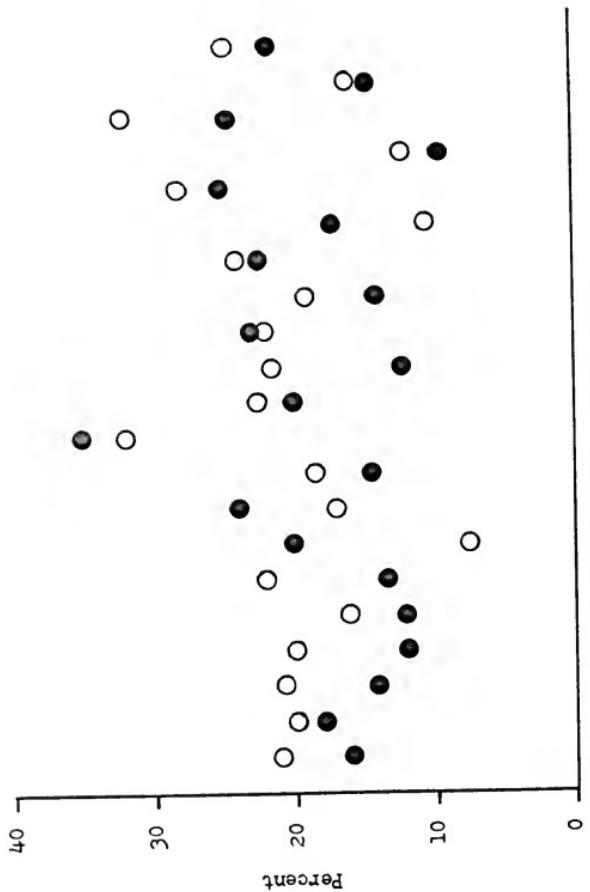
$T_4$  = serum thyroxine in  $\mu\text{g}/100 \text{ ml serum}$ .

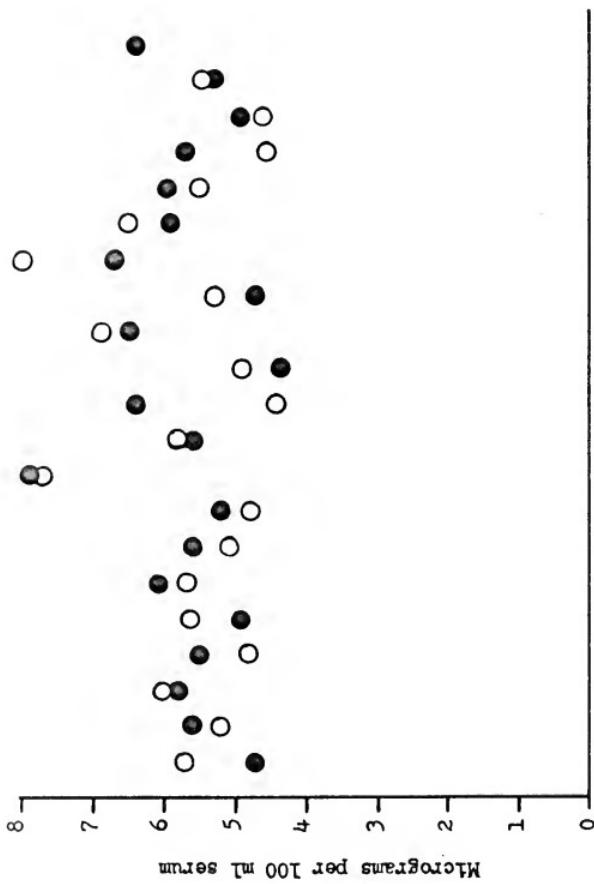
RAI = radioactive iodine uptake in percent.

Total subjects = 22; 18 female and 4 male.

#### Aesthetic Considerations

Tastes and Odors - Iodine did not create any objectionable tastes or odors during this study. Its vapor pressure (0.31 mm of mercury) is





○ Values prior to iodination of the water.  
● Values after swimming for one month in iodinated pool for three hours per week.

Fig. 41 - Effect of Swimming for One Month in Water Containing 5 ppm Iodine on FBI.

only about 1/17,000 that of chlorine (5300 mm of mercury), which means that iodine residuals in the concentrations required for swimming pools are detected only by experienced observers, if at all.

Color - Iodine residuals in concentrations varying from 0.60-1.0 ppm impart a light green to deep emerald green color to the water in most pools. This is the first noticeable difference between iodinated pools and chlorinated pools and the one which receives the most adverse comment, usually by the females present. This green color is not objectionable and resembles the color of the water found around the Florida Keys and throughout the Bahamas. Turbidity and the color of the pool have a great effect on this color. This color may be controlled to a certain degree by maintaining the pH and the iodide ion concentration at the most favorable values for minimum color formation. This means maintaining the iodine residual primarily as hypoiodous acid instead of elemental iodine, since the hypoiodous acid ( $\text{HIO}$ ) is colorless, whereas elemental iodine ( $\text{I}_2$ ) is highly colored. Calculations from the hydrolysis reaction will demonstrate this method of color control.



$$K_h = 3 \times 10^{-13} \text{ at } 25^\circ\text{C}$$

$$\frac{[\text{HOI}]}{[\text{I}_2]} \cdot \frac{[\text{H}^+]}{[\text{I}^-]} = K_h \quad (19)$$

$$\frac{[\text{HOI}]}{[\text{I}_2]} = \frac{K_h}{[\text{H}^+] [\text{I}^-]} \quad (20)$$

At pH 8.0 and an Iodide concentration of 4 ppm

$$\frac{[\text{HOI}]}{[\text{I}_2]} = \frac{3 \times 10^{-13}}{1.58 \times 10^{-8} \quad 1.58 \times 10^{-5}} = 0.95 \quad (21)$$

At pH 8.0 and an Iodide concentration of 1 ppm

$$\frac{[HOI]}{[I_2]} = \frac{3 \times 10^{-13}}{1 \times 10^{-8} \quad 7.88 \times 10^{-6}} = 3.81 \quad (22)$$

Equations (18) through (22) show that by decreasing the iodide ion concentration the ratio of colored form to colorless form may be decreased to one-fourth of its former value. Figure 42 presents data for this ratio for different iodide concentrations at different pH values. In this particular pool it was very noticeable when iodine was being released by the chlorine at each of the four inlets, as a distinct brown spot was visible immediately above the inlets. These brown spots led to some adverse comments, but in a pool with adequate recirculation and the continuous release of iodine the color can be maintained at a pleasant light green in the shallow end to a deep aquamarine green in the deep end by keeping the pH at about 7.8 and the iodide ion concentration of not over 2.0 parts per million in addition to the desired elemental iodine residual.

#### Bather Acceptance

Even though the poor circulation resulted in occasional transitory brown areas in the pool, the results of a poll to evaluate bather acceptance are interesting. Questionnaires were handed out on the 5th, 6th, and 7th day following the end of the test period, and when  $Cl_2$  was again being employed to determine if the swimmers preferred one disinfectant over the other. The pool was operated exactly as during the iodine disinfection period. The water temperature dropped about  $1.5^{\circ}C$  during the week which caused a few swimmers to indicate that the iodine

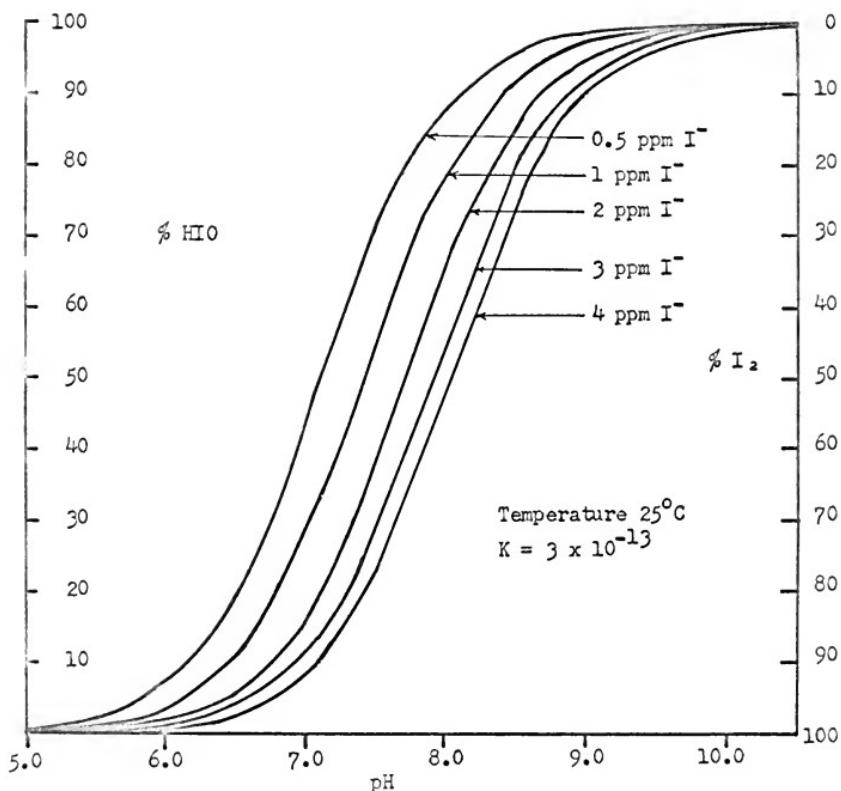


Fig. 42 - Effect of Concentration of Iodide Ion on Molecular Ratios  $[\text{HIO}] / [\text{I}_2]$  at Various pH Values. These Calculations Neglect Some Decomposition of HIO Which Takes Place at pH Values Above 9.0.

made the water feel warmer, but this temperature change was due to lower air temperatures and some heavy rains which fell during the week.

Many people provided full statements expressing their preference for one or the other of the two halogens. Others simply checked a prepared form with no comment as to why they preferred one over the other. Several different factors were mentioned as the basis for preference. Eye and nose burn and color received the most attention. Others, such as odor, taste, and feel were mentioned by a few bathers. Nine swimmers noted effects of one or the other of the halogens on hair, jewelry or swim suits. Table 22 is a tabulation of the questionnaire data. Tables 23 and 24 tabulate the individual preferences expressed by members of the group. Figure 43 is a graphical presentation of these data. A sample questionnaire is shown on page 114.

Table 22  
Swimming Pool Questionnaire Data

		<u>Percent Total</u>
Total questionnaires completed	154	100
Preference expressed	147	95.5
Preference for Cl <sub>2</sub>	82	53.2
Preference for I <sub>2</sub>	65	42.3
No preference	7	4.5

Table 23

Reasons Mentioned for Preference of Cl<sub>2</sub> Over I<sub>2</sub>

Sex	Physical Considerations			Aesthetic Considerations		
	Eyes	Nose	Color	Odor	Taste	Feel
M	14	3	30	4	4	3
F	12	0	16	5	3	2

Note: The factor most often mentioned by those people preferring Cl<sub>2</sub> over I<sub>2</sub> was the color. Most felt that the blue color present when Cl<sub>2</sub> is properly added was more pleasing than the light green of the I<sub>2</sub>. Some women preferred Cl<sub>2</sub> even though Cl<sub>2</sub> burned their eyes severely.

Table 24

Reasons Mentioned for Preference of I<sub>2</sub> Over Cl<sub>2</sub>

Sex	Physical Considerations			Aesthetic Considerations		
	Eyes	Nose	Color	Odor	Taste	Feel
M	29	4	5	1	2	2
F	22	1	7	1	2	3

Note: The factor most often mentioned by these people preferring I<sub>2</sub> to Cl<sub>2</sub> was the absence of eye burn. These people had previously suffered eye burn from Cl<sub>2</sub> and much preferred the I<sub>2</sub> to the Cl<sub>2</sub>.

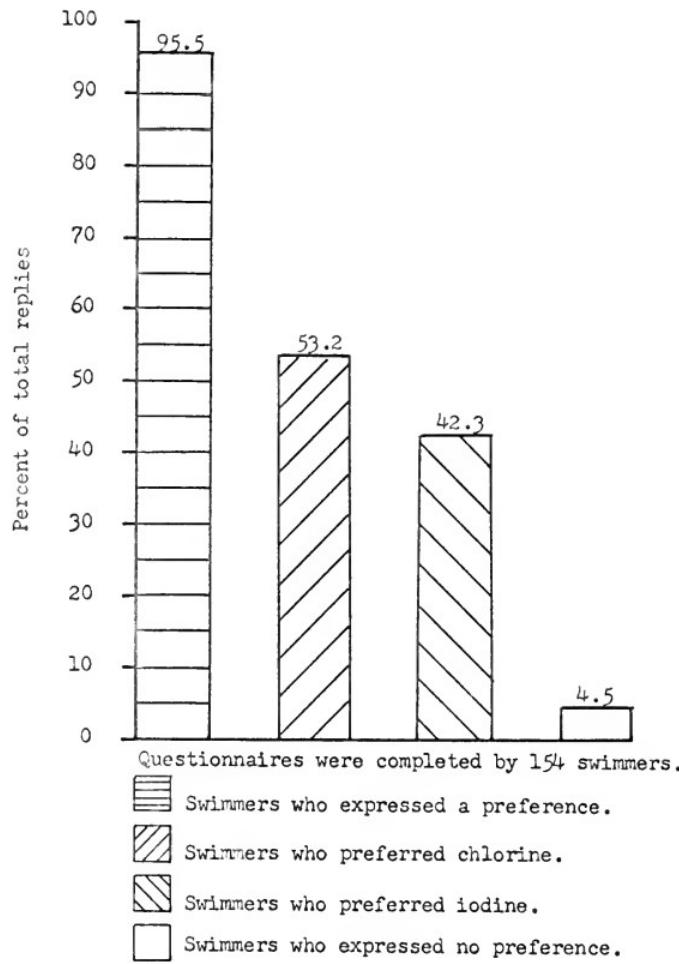


Fig. 43 - Swimmer Disinfectant Preference. University of Florida Swimming Pool, Summer of 1964.

SAMPLE QUESTIONNAIRE

Swimming Pool Study

Name \_\_\_\_\_

Age \_\_\_\_\_

Sex \_\_\_\_\_

Date \_\_\_\_\_

Which do you prefer:

Pool Containing Iodine (      ) Pool Containing Chlorine (      )

Why? \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

Disinfection Cost

The swimming pool used in this study did not then conform to good design criteria for adequate recirculation and disinfection. Therefore, a comparison of cost data employing the two halogens would probably be even more favorable to  $I_2$  in properly designed pools.

Many of the properties of iodine become significant in reducing the cost of swimming pool disinfection. Its low vapor pressure, stability under ultraviolet light, stability in the presence of ammonia, negligible effect on pool pH and most important the reuse of the iodide ion all combine to reduce the cost of swimming pool disinfection even though elemental iodine costs approximately \$1.16 per pound and chlorine costs 10 to 12 cents per pound in 150 pound cylinders. Figure 44 illustrates the stability of iodine residuals compared to the stability of chlorine residuals in a swimming pool. The iodine was released from potassium iodide by means of gaseous chlorine during most of this study.

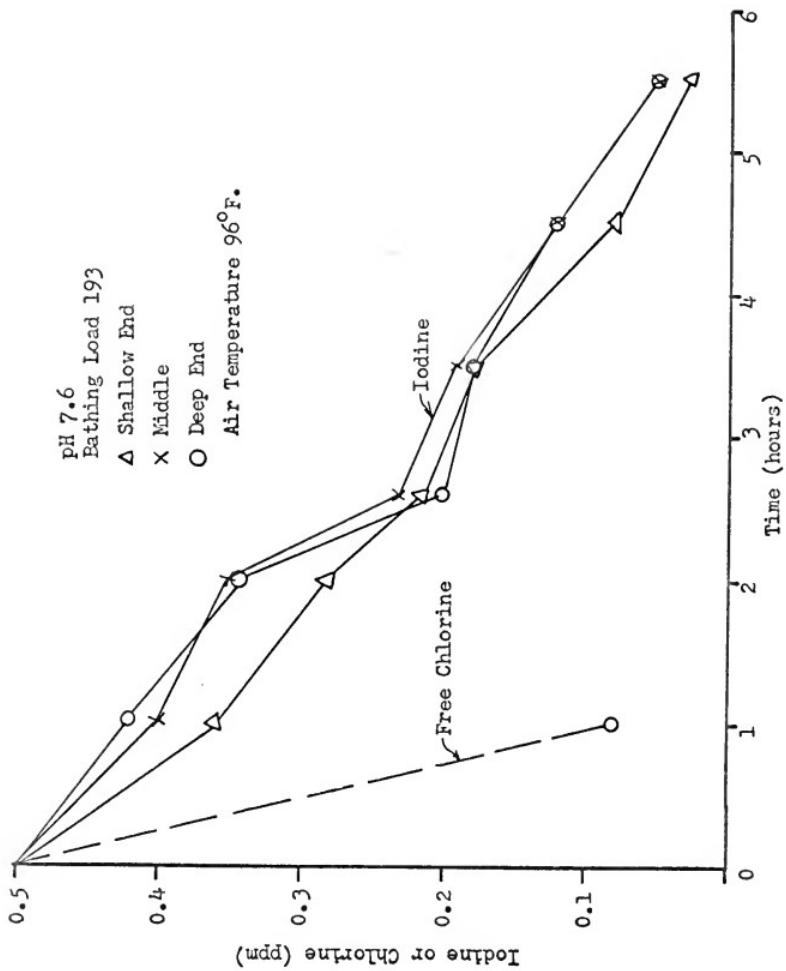


Fig. 44 - Iodine and Chlorine Demand Curves for Water from the University of Florida Swimming Pool, June 1964.

Commercial grade muriatic acid was used to control pH during the iodination period and sodium carbonate was used during the chlorination period. The iodine data are based upon 25 days of operation and the chlorine data are based on only 5 days of operation. The water temperature was higher during the iodination period than during the week of chlorination, because of higher air temperatures during the iodination period and because of some heavy rain during the chlorination period.

Figure 45 presents a cost comparison for the two periods of disinfection. The cost of disinfection and pH control was \$4.70 per day during the iodination period and \$7.98 per day during the chlorination period. If sodium iodide could have been used at a cost of \$1.10 per pound, the cost per day for iodination would have been reduced still further to \$3.72 per day. The short period of only five days during which cost data for I<sub>2</sub> were obtained was not sufficient to make an adequate comparison of cost data possible. However, the very large difference between the two values obtained, together with results from other pool tests over a much longer period of time definitely establish the fact that under proper operating conditions, disinfection of a swimming pool with iodine can be carried out at substantially less cost than with chlorine.

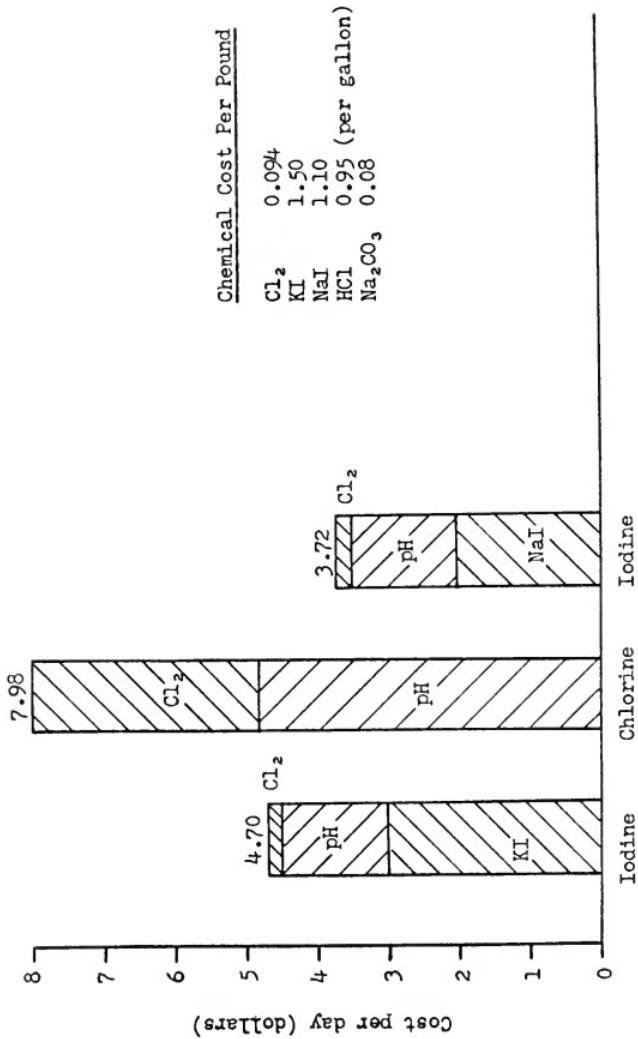


Fig. 45 - Cost of Swimming Pool Disinfection. University of Florida Swimming Pool, June 16, 1964 to July 17, 1964.

Laboratory Study Section

Saturator Design

At the beginning of this project three possible ways of preparing an iodine solution of suitable strength and in adequate quantity for disinfecting water were considered. The first envisioned an iodine saturator operated in conjunction with a solution tank in order to offset peak feed requirements and a feed pump. The second possibility was to heat iodine crystals and use an eductor to feed the iodine vapor into the water. A third possibility, the one actually used and in use at the present time, was to build the iodine saturator of such size and capacity that a sufficient quantity of saturated iodine solution is always stored and available within the saturator itself to meet any dose requirements placed on the system and to feed directly from the saturator into the raw water. There were no data available for long-term application of any of these possibilities.

Behrman<sup>51</sup> experimented with both screened and unscreened iodine crystals in a small iodine saturator (1-1/8" I.D. glass tube 24" long) with Chicago tap water in 1959. His results for the Chilean crude iodine (unscreened) are presented in Table 25. His data show that iodine solutions of sufficient strength for water disinfection can be prepared by simple percolation of water through a bed of elemental iodine crystals. He experienced difficulty with air binding of some of the iodine beds and also bed separation. He attributed this to the quantity of air in the Chicago tap water, which is frequently "super-saturated" with air. He did not operate his saturators for the great

Table 25

Effect of Bed Depth and Rate of Flow on Rate of Solution  
of Elemental Iodine  
(after Behrman)

Direction of Flow	Bed Depth (inches)	Flow Rate g/m/ft <sup>2</sup>	Temperature °C	I <sub>2</sub> ppm	Percent Saturation
Down	3	29	22.5	186	59.1
Down	3	18.4	23.5	226	69.5
Down	3	7.9	24	283	85.8
Down	3	3.8	23.5	306	94.2
Up	3*	24.2	23	212	66.2
Up	3*	18.4	23	206	64.4
Up	6*	4.1	23	336	105
Up	6*	7.8	23	317	98.9
Down	6	14	23.5	312	96.2
Down	6	8.0	23	314	98.2
Down	6	3.84	23	325	101
Down	12	7.6**	24.5	348	104
Up	12	10.3	26.5	378	108
Up	12	3.84	27.5	381	103

\*Bed divided by layer of separated air; top portion raised like piston.

\*\*Maximum; rapid reduction of flow due primarily to separation of air.

length of time which would be required in actual routine water disinfection. Black<sup>33</sup> used a small iodine saturator and eductor for swimming pool water disinfection and found it feasible.

It was decided that an iodine saturator feed arrangement would be the easiest to design, build, test, and put into operation in the shortest time. It was imperative to initiate iodination as quickly as possible in order that long term physiological data could be developed. Accordingly, a 6" I.D. vitrified clay pipe 24" long was fashioned into an iodine saturator employing a 14" bed of 4 mesh Chilean crude iodine crystals. See Figure 46. The bottom was sealed with glass, paraffin and reinforced concrete. Inlets and outlets were 3/8" I.D. stainless steel type 304. The bed support system consisted of 6" of glass marbles, 0.3" of 6 mm glass beads and 0.6" of 4 mm glass beads. This saturator was tested with demineralized water first and then with Lowell water. At the rate of 40 gallons per hour the strength of the iodine solution was almost always 100% of saturation, using either the Lowell water or demineralized water. These initial tests were conducted by allowing the water to flow by gravity through the bed from five gallon plastic carboys with only about 3" of head above the iodine bed. Typical values in terms of percent of saturation are shown in Table 26.

A second saturator was constructed on the basis of information gathered from the operation of the first saturator. This saturator was designed to handle the feed requirements at Station No. 2 at the Men's Prison, which it did during the first year of iodination. It was then replaced with a Saran-lined steel saturator.\* A second saturator was

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\*A product of Dow Chemical Company, Midland, Michigan.

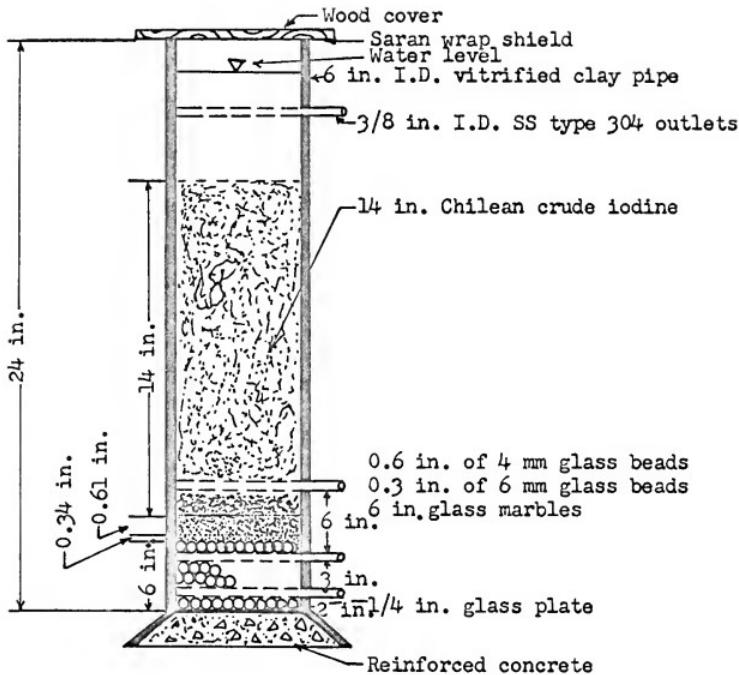


Fig. 46 - Experimental Iodine Saturator No. 1. Completed September 7, 1963.

Table 26  
Typical Iodine Solution Strengths from Saturator No. 1

Temperature	Direction of Flow	Theoretical Solubility	Flow Rate	I <sub>2</sub> ppm	Percent Saturation
21.5° C	Down	305 ppm	40 g/hr	304	99.6
23 ° C	Down	320 ppm	40 g/hr	318	99.4
24 ° C	Down	330 ppm	40 g/hr	326	98.8

fashioned from a 3' section of 8" I.D. vitrified clay pipe. An 18" bed of iodine crystals was used in this saturator to provide an added safety factor. See Figure 47. This second saturator was placed in a test stand in the laboratory and connected to one of the iodine feed pumps and the constant level device, and pumped for 41 hours at 12 gallons per hour. The pumping rate was then increased to 40 gallons per hour which was higher than that required at Station No. 2. Throughout some 85 hours of pumping at rates as high as 55 gallons per hour, the saturation values remained above 95% of the expected values. Each of the feed pumps was connected to this saturator and pumped for several hours in the laboratory. There was no evidence of bed packing or air binding in any of these tests.

The third saturator was constructed to duplicate this one with the following exceptions. It was made from a 10" I.D. 5' long vitrified clay pipe and has a 24" deep bed of elemental iodine crystals. In

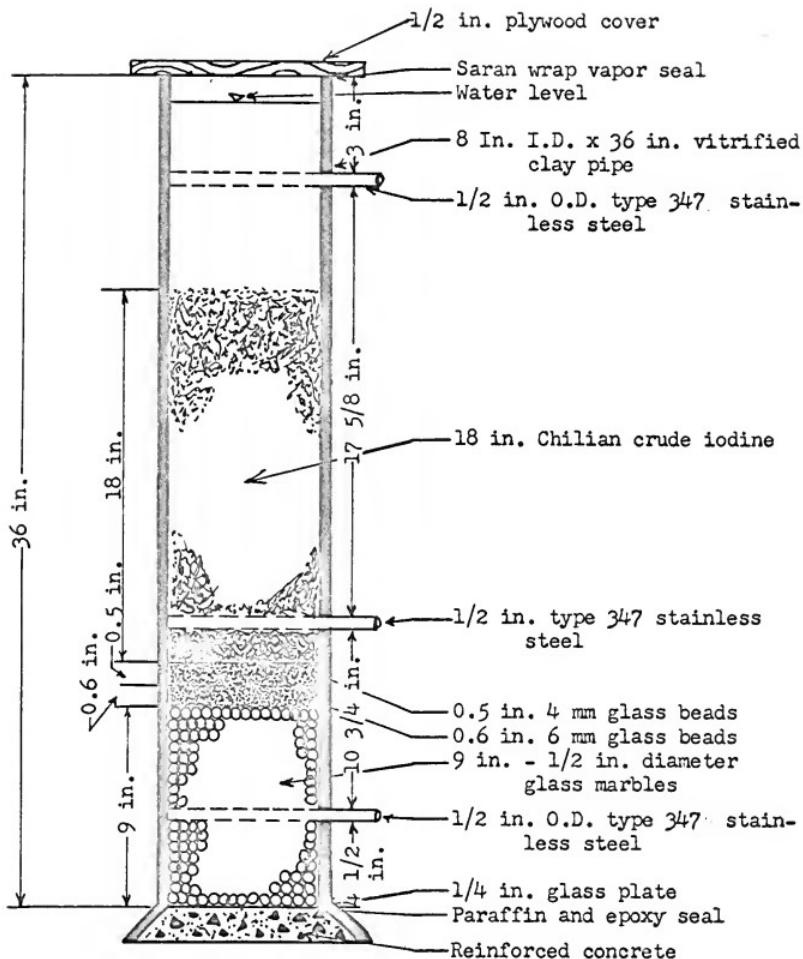


Fig. 47 - Experimental Iodine Saturator No. 2 Completed October 4, 1963.

addition, the support system varies somewhat. See Figure 14. It was constructed in place at Station No. 1 and placed in operation on October 28, 1963, and is still functioning perfectly. This saturator supplies iodine for approximately 100,000 gallons of raw water per day at a dosage of 1.00 ppm.

Saturators No. 4 and No. 5 are identical in operation to No. 3 except that the saturator body is made of steel and lined with Saran. Saran-lined steel pipe up to 8" I.D. is a commercially available item from the Dow Chemical Company. One of these saturators has been in operation at Station No. 2 for over eight months. See Figure 48.

#### Discussion

These saturators described above have provided saturated iodine solution continuously for over 22 months. Throughout this entire period the iodine concentration has continuously been 95% or better of the expected value from the iodine solubility curve. Refer to Figure 12. Table 27 illustrates the percentage of saturation of random monthly samples.

One problem has arisen from the use of vitrified clay pipe for the saturator body. Vitrified clay pipe is sometimes porous and iodine solution will percolate through the pipe wall. Only one of the three vitrified clay saturators has been sufficiently porous to create problems from leakage of iodine solution. This saturator was replaced after one year of service with the Saran-lined steel saturator.

In order to determine if the leakage of iodine solution from the

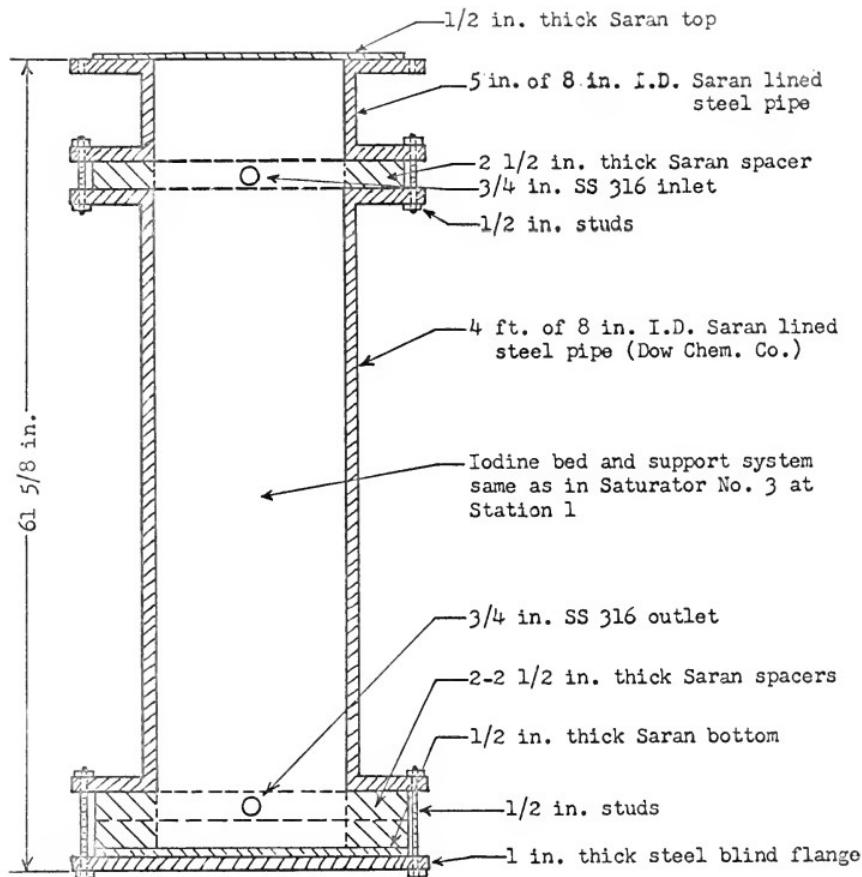


Fig. 48 - Experimental Iodine Saturator No. 4 Completed March 4, 1964  
and Installed at Station 2 on January 7, 1965.

Table 27

Concentration of Random Monthly Samples from Saturators

Date	Temperature °C	Iodine Concentration (ppm)	Iodine Solubility (ppm)	Percent Saturation
Nov. 1963	21.5	293	305	96.2
Dec.	21.5	291	305	95.5
Jan. 1964	21.5	296	305	97.1
Feb.	21.5	290	305	95.1
Mar.	21.5	290	305	95.1
Apr.	21.5	290	305	95.1
May	22	305	310	98.2
June	22	304	310	98.1
July	22	304	310	98.1
Aug.	22	295	310	95.2
Sept.	22	297	310	95.7
Oct.	22	300	310	96.8
Nov.	22	298	310	96.2
Dec.	21.5	292	305	95.7
Jan. 1965	21.5	304	305	99.6
Feb.	21.5	291	305	95.5
Mar.	21.5	293	305	96.1
Apr.	21.5	297	305	97.3
May	22	297	310	95.7
June	22	300	310	96.8

clay pipe saturators might cause a structural failure of the pipe, Saturator No. 1 was sacrificed. The following statements reflect the condition of the saturator after 13 months and 21 days of service.

Experimental Saturator No. 1 - September 7, 1963 - October 29, 1964

1. Saturator body - The saturator body consisted of a 6" I.D. vitrified clay pipe 24" long (shop item). The vitrified clay pipe used for the saturator body did not show any effect whatsoever after the period of 13 months and 21 days of service.
2. Saturator bottom - The bottom was constructed of a very rich mixture of reinforced portland cement concrete plus a 1/8" thick glass plate. The junction of the glass and the pipe was sealed with paraffin. The cement was moisture-cured for several days.

The bottom did not show any effect from the iodine solution. Bond between the concrete and clay pipe was not altered in any way. The paraffin was still intact although it had absorbed sufficient iodine to color it deeply.

3. Iodine bed support - The bed support consisted of a 6" thick layer of ordinary glass marbles. The filter on top of the bed support was made up of layers of solid glass beads of 4 mm and 6 mm diameter. As expected, the glass marbles and glass beads were not affected.

4. Iodine bed - The iodine bed consisted of commercial grade elemental iodine of 99.9% purity. The iodine was not processed in any way, but was added directly to the saturator from its shipping container.

The iodine bed was replaced as iodine was used, a simple operation presenting no problems to the operator.

5. Saturator piping - The iodine saturator piping consisted of 3/8" I.D. thick walled stainless steel tubing, type 304. The piping exposed to the saturated iodine solution of about 300 mg/l was not visibly affected. The piping in contact with pure elemental iodine suffered severe corrosion and total deterioration. Stainless steel (type 304) will not withstand iodine vapor or iodine crystals.

6. Saturator top - The top of the saturator consisted of a seal of Saran wrap of the type commonly sold for household use in grocery stores and a cover of 3/4" thick plywood. The plywood holds the Saran wrap in place. The Saran (Dow Chemical Company) vapor seal works very well. Some iodine vapor was adsorbed on the surface of the Saran, but the Saran was unaffected.

7. Piping sealer - The space between the saturator itself and the saturator piping was sealed with epoxy type glue made by the Devcon Company. The epoxy glue withstood the saturated iodine solution satisfactorily, but is rapidly attacked by iodine vapors.

The vitrified clay pipe used in the construction of this first large iodine saturator was purchased at an ordinary building material supply house. The surfaces of the pipe were not lined or altered in any way. This pipe was shaped by an extrusion process, utilizing pressures of 125 psi, or more. Then the clay was glazed with NaCl vapor at 2000°F. This process produces a very chemically resistant material, which on the basis of this first experimental iodine saturator withstood elemental iodine extremely well.

The internal structure of the pipe wall is very porous and

striated. These striations are probably due to trapped air in the clay at the time of manufacture. If the internal surface of the pipe is ruptured, the iodine solution will enter the pipe wall and follow these openings to the outside. In this particular section of pipe the internal surface was not ruptured and hence there was no leakage of iodine solution from the saturator. In the second saturator, constructed very similar to this one, leaks did develop. Evidently, both the interior surface of the pipe and the exterior surface of the pipe were porous. The iodine solution simply followed the passageways to the outside. Following more than 13 months of continuous service, this pipe was cut in both the horizontal and the vertical directions by means of a "Skil" saw mounted with a masonry blade. No evidence was found to indicate any change in the properties of this vitrified clay pipe after the 13 month-plus exposure to elemental iodine and iodine solution.

The method used to seal the bottom works very well. The cement was still bonded very firmly to the pipe wall and the paraffin, although permeated with iodine, was still in place. There was no leakage through the bottom. The iodine in the paraffin was solvent extractable.

The glass marbles and glass beads were in the same condition as when they were placed in the saturator. Some iodine was adsorbed on the surface of the glass, but there was no visible evidence of damage.

The stainless steel outlets at the bottom of the saturator showed no signs of corrosion or deterioration. These outlets were submerged in iodine solution only. The two top outlets were in direct contact with the elemental iodine crystals in addition to the saturated solution and

were completely deteriorated. This points out the need for a very inert material to be used in contact with the elemental iodine crystals.

The vapor seal made of Saran wrap was very effective. This particular saturator was used in the laboratory and was constantly vapor tight.

No damage to the epoxy-type glue was attributed to the saturated iodine solution, but the pure iodine vapor caused the glue to become dark colored and very brittle. Iodine vapor destroyed the bonding qualities of the glue.

The total cost of the necessary materials required to build such a saturator is less than \$30.00. The service life of such a saturator is not known at this time since of the two initially constructed and installed, one is still in service after almost two years of continuous use. The vitrified clay pipe would last indefinitely. The stainless steel, exposed only to saturated iodine solution, would probably last for many years. The service life of the epoxy-type glue is probably several years, since after two years of continuous exposure to a saturated iodine solution, it appears to be unaffected.

#### Determination of the Iodine Demand of Water from the Three Wells at Lowell

##### General Discussion

The halogen demand of a water must be satisfied before a disinfecting residual can be obtained. This demand may be defined as the difference between an applied dose of halogen and the residual remaining at a given time. Organic and inorganic reducing agents react with and

destroy free halogen residuals. Hydrogen sulfide and other reducing agents are found in some water supplies and add to the halogen demand. Due to its greater chemical activity and higher oxidation potential, the chlorine demand of water is usually outstandingly higher than the iodine demand. In most cases, the greater the pollutional load of the water the greater will be the difference between the chlorine demand and the iodine demand of a water.

Since there is no natural or developed surface drainage in the Lowell area, the effluent from the two sewage treatment plants is recharged into the underground aquifers. This has been done for many years. The presence of enteric organisms in more than 50% of all samples from Well No. 2 undoubtedly results from this practice. Iodine demands have been run routinely on all three wells to indicate any gross change in water quality since the study was initiated.

#### Experimental Technique

##### Reagents

Standard iodine and chlorine solutions containing 1000 mg/l were prepared and standardized according to STANDARD METHODS by the starch-iodide procedure and stored in brown glass bottles. Standard phenyl-arseneoxide (.00564 N) was prepared and standardized according to STANDARD METHODS.

Solution pH was determined with a Beckman Model 6 pH meter. All iodine and chlorine residuals were determined with a Wallace and Tiernan amperometric titrator and using standard phenylarseneoxide solution.

Procedure

The raw well water was collected in five gallon polyethylene containers and the demand studies were set up within two hours after sample collection. Two liter samples were placed in acid-washed, brown glass bottles. Measured dosages of iodine were added and the solutions thoroughly stirred. Two hundred milliliter samples were withdrawn at predetermined time intervals and halogen residuals determined. The amperometric titrator was sensitized for iodine by the method of Kramer et al.<sup>52</sup> The electrode was immersed in iodine solution overnight and five titrations were run on the titrator before the actual test began. Kramer reported an accuracy of  $\pm$  0.01 parts per million for a 1.00 parts per million initial dose. Duplicate samples were run in all cases.

Discussion of Results

The data in Tables 28, 29 and 30 indicate that when the project was initiated in 1963, Well No. 2 was the worst well in terms of iodine demand. The bacteriology was consistent with these data. Well No. 3 at this time had the least iodine demand and the best bacteriology. In 1964, both Wells No. 1 and No. 2 deteriorated in water quality as evidenced by slight increases in iodine demand. Well No. 3 remained unchanged at this time, but in 1965 it had an increase in iodine demand and an increase in the number of bad bacteriological samples. Wells No. 1 and No. 2 have had a decrease in iodine demand in 1965, and have produced better quality water, with fewer unsatisfactory bacteriological

samples than in previous months. Figures 49, 50, and 51 graphically present the data shown in Tables 28, 29, and 30, and Figure 52 shows both the chlorine and the iodine demands of water from each of the three wells.

Table 28

Typical Iodine Demand of Water from Three Wells, May 1963

Well	I <sub>2</sub> Dose ppm	1 Hour Demand ppm	2 Hour Demand ppm	4 Hour Demand ppm	24 Hour Demand ppm
No. 1	1.00	0.18	0.18	0.25	0.63
No. 2	1.00	0.18	0.30	0.43	0.75
No. 3	1.00	0.10	0.18	0.27	0.35

Table 29

Typical Iodine Demand of Water from Three Wells, May 1964

Well	I <sub>2</sub> Dose ppm	1 Hour Demand ppm	2 Hour Demand ppm	4 Hour Demand ppm	24 Hour Demand ppm
No. 1	1.00	0.25	0.34	0.43	0.75
No. 2	1.00	0.32	0.43	0.53	0.83
No. 3	1.00	0.10	0.12	0.17	0.39

Table 30

Typical Iodine Demand of Water from Three Wells, May 1965

Well	I <sub>2</sub> Dose ppm	1 Hour Demand ppm	2 Hour Demand ppm	4 Hour Demand ppm	24 Hour Demand ppm
No. 1	1.00	0.21	0.22	0.25	0.53
No. 2	1.00	0.25	0.25	0.27	0.57
No. 3	1.00	0.11	0.16	0.26	0.57

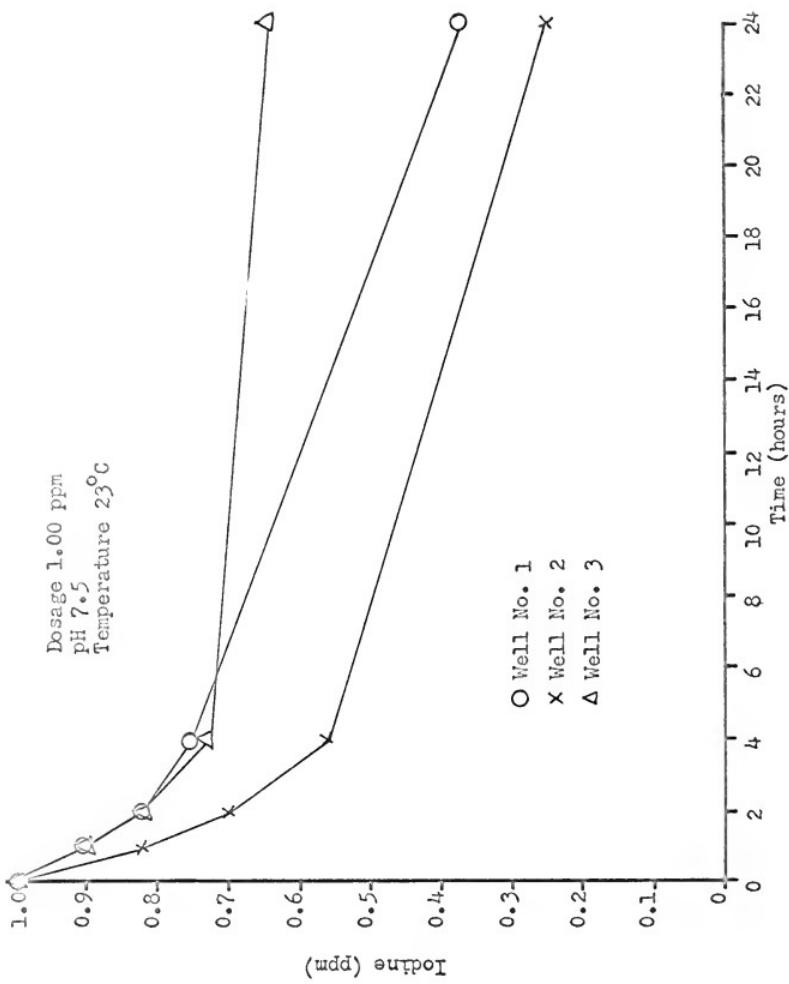


Fig. 49 - Iodine Demand Curve of Lowell Well Water (May 1963).

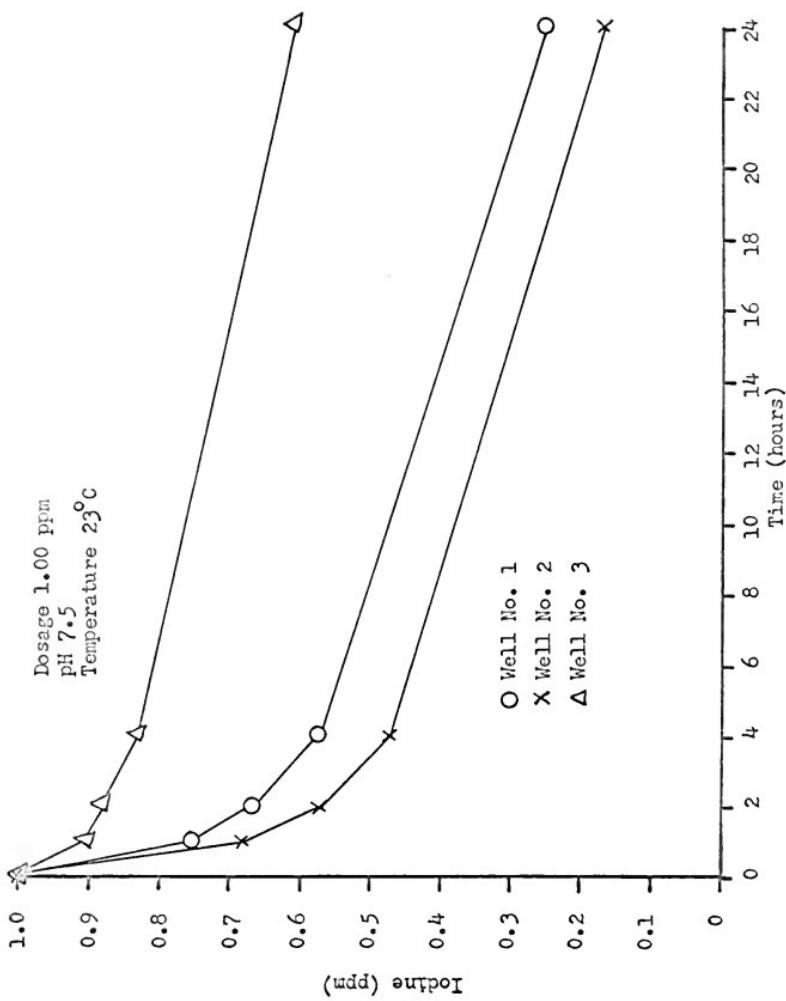


Fig. 50 - Iodine Demand Curves of Lowell Well Water (May 1964).

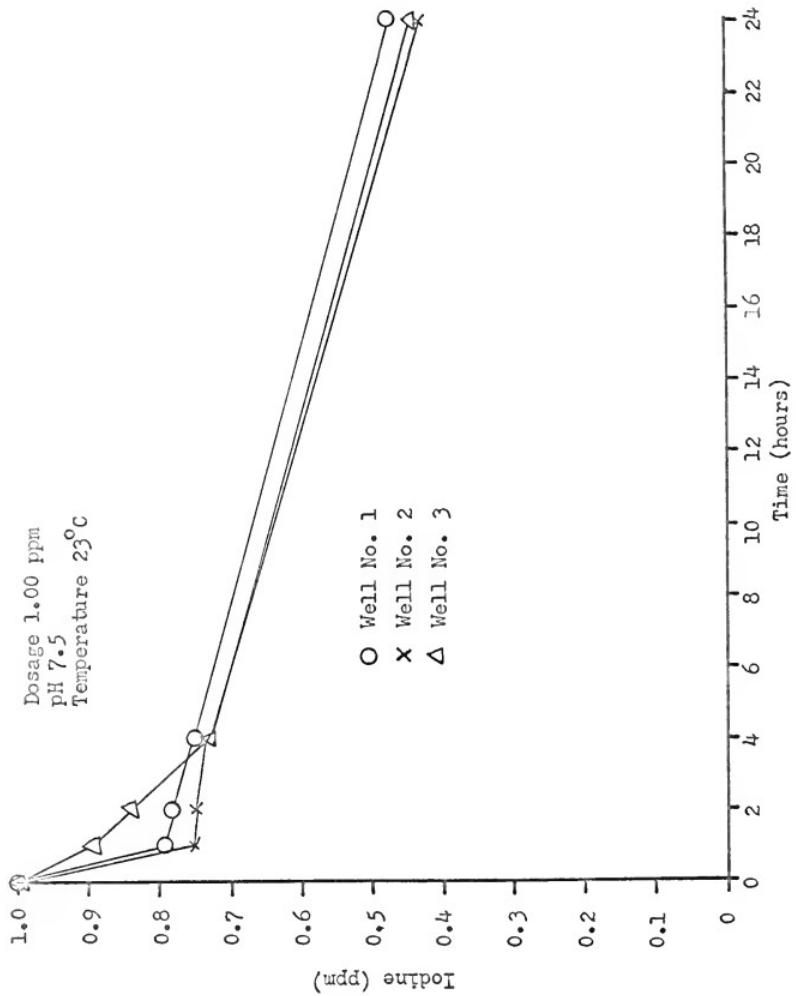


Fig. 51 - Iodine Demand Curves of Lowell Well Water (May 1965).

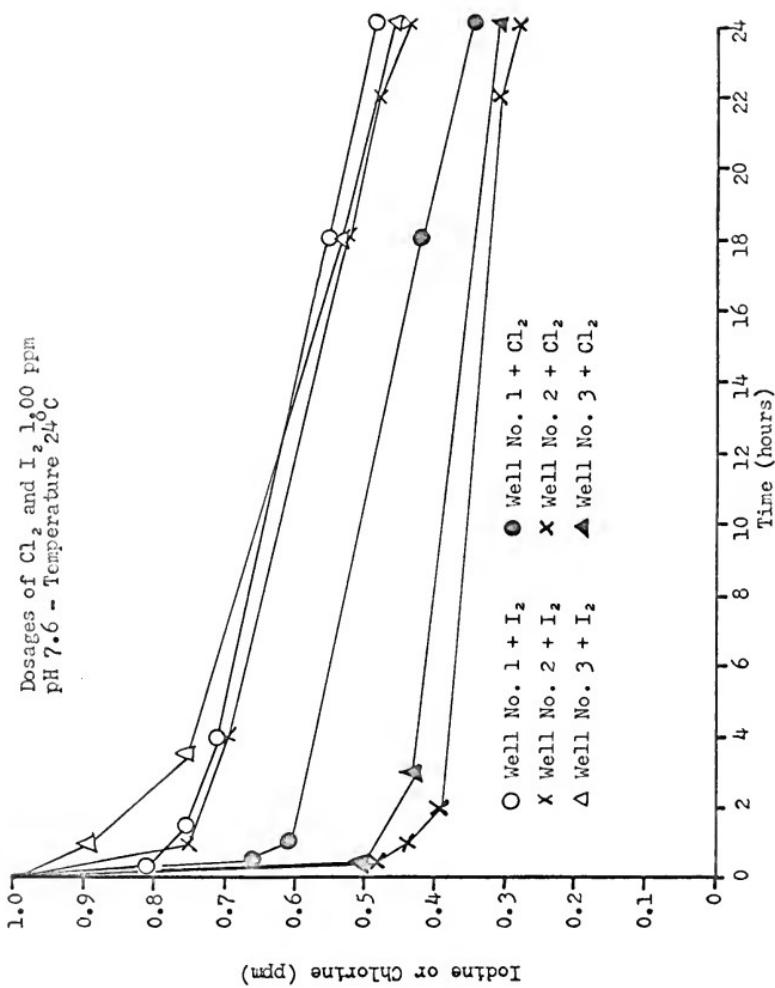


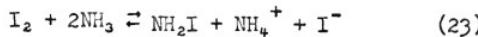
Fig. 52 - Chlorine and Iodine Demand Curves of Lowell Well Water.

### The Effect of Ammonia in Iodine Disinfection

#### General Discussion

One of the primary disadvantages of chlorine is its ability to form chloramines in the presence of ammonia or nitrogen containing organic compounds. This chloramine formation takes place almost instantaneously and the resultant compounds are relatively ineffective germicides, being on the order of 1/30th as effective as free chlorine.<sup>44</sup> Iodine, on the other hand, does not react with ammonia in dilute aqueous solutions. This stability is demonstrated in swimming pool disinfection, where iodine is far more stable in the pool water than chlorine as illustrated in Figure 53.

In 1952, McAlpine<sup>45</sup> suggested that a colorless iodoamine exists according to the following reaction



$$K = \frac{[NH_2I][NH_4^+][I^-]}{[I_2][NH_3]^2} \quad (24)$$

K from 1.2 to 2.6

He based the occurrence of this reaction on the decolorization which takes place when 50 ml of 0.01 N KI<sub>3</sub> solution was added to 200 ml of 0.01 N NH<sub>3</sub>. These solutions are much more concentrated than the 1 x 10<sup>-6</sup> molar iodine solutions encountered in water disinfection and the pH of the solution was not given in these studies. A 0.01 N ammonia solution has a pH above 10.0 and hypoiodous acid is formed in aqueous iodine solutions at high pH values which would be in part

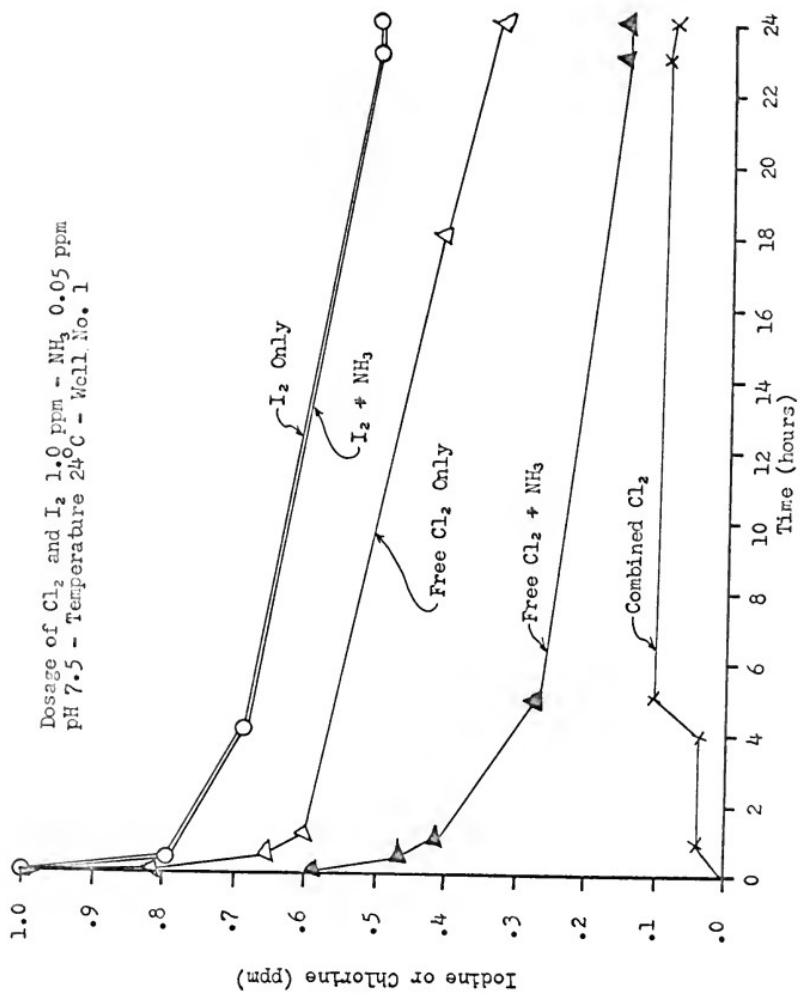


Fig. 52 - Effect of Added  $\text{NH}_3$  on Type and Persistence of Chlorine and Iodine Residuals.

converted to hypoiodate and, in time, to iodate, all of which are colorless. A study was initiated to investigate the stability of iodine in the presence of ammonia and to compare its stability with that of chlorine under the same conditions.

#### Experimental Techniques

##### Reagents

A stock solution of ammonium sulfate was prepared to furnish one milligram of NH<sub>3</sub> per milliliter of solution. Standard iodine and chlorine solutions were prepared as before. Standard phenylarseneoxide solution (.00564 N) was the titrating reagent as before.

##### Procedures

Carefully measured volumes of the standard NH<sub>3</sub> solution were added to water from Lowell Well No. 1, and stored in brown bottles. Measured volumes of standard halogen residuals were added to these samples and halogen residuals carefully determined at predetermined intervals. The data are presented in Tables 31 and 32, and Figures 54 through 56 illustrate the rapid formation of chloramine, the rapid disappearance of free chlorine in the presence of ammonia, and the stability of iodine in the presence of ammonia.

##### Discussion of Results

These data show that ammonia has no effect on the iodine demand of a water under routine operating conditions. Ammonia in concentrations up to 0.4 parts per million did not affect the iodine demand after 15, 30, or 60 minutes or even after 24 hours. These same ammonia concentrations caused a drastic increase in the chlorine demand.

Table 31  
Effect of Added Ammonia on Iodine Demand

NH <sub>3</sub> ppm	I <sub>2</sub> ppm	pH	Temper- ature 0°C	15 Minute Demand ppm	30 Minute Demand ppm	1 Hour Demand ppm	24 Hour Demand ppm
.05	1.00	7.5	24	0.15	0.18	0.21	0.55
0.10	1.00	7.4	24	0.18	0.18	0.25	0.53
0.15	1.00	7.4	24	0.12	0.18	0.21	0.57
0.20	1.00	7.6	23	0.11	0.18	0.21	0.43
0.40	1.00	7.6	23	0.07	0.13	0.14	0.40

Table 32  
Effect of Added Ammonia on Chlorine Demand

NH <sub>3</sub> ppm	Cl <sub>2</sub> ppm	pH	Temper- ature	15 Minute Demand	30 Minute Demand	1 Hour Demand	24 Hour Demand ppm
.05	1.00	7.5	24	0.63	0.70	0.70	0.87
0.10	1.00	7.4	24	0.68	0.78	0.86	1.00
0.15	1.00	7.4	24	0.64	0.64	0.75	0.85
0.20	1.00	7.6	23	1.00*	*	*	*
0.40	1.00	7.6	23	1.00*	*	*	*

\*No free available chlorine after 15 minutes.

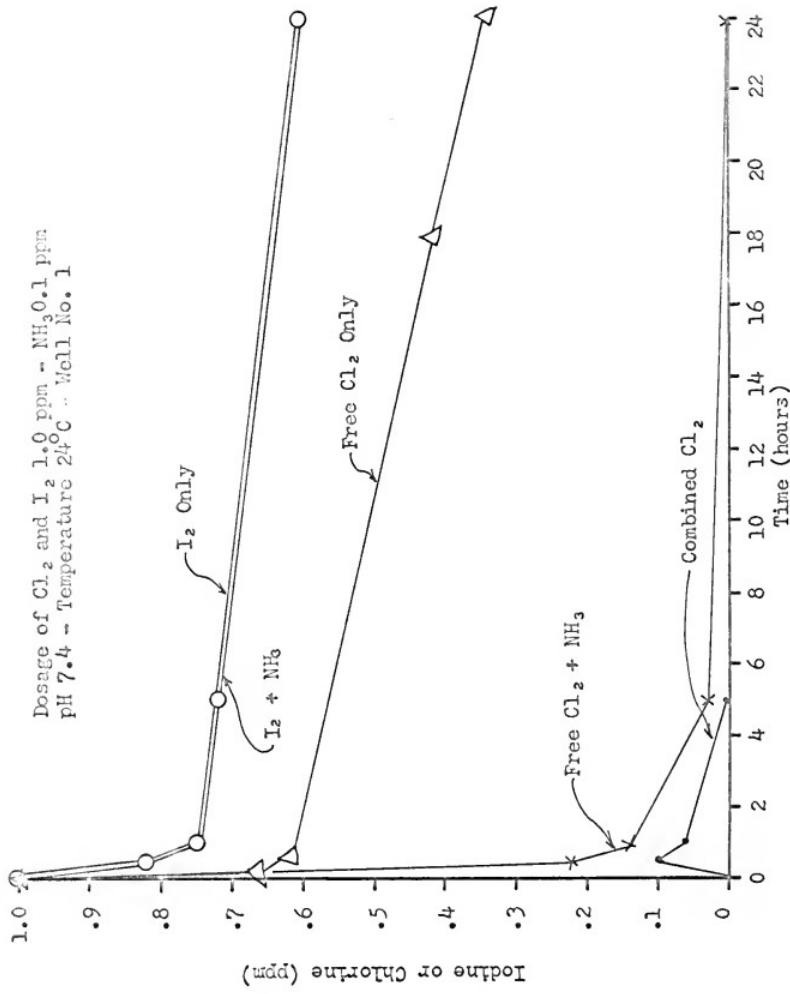


FIG. 54 - Effect of Added  $\text{NH}_3$  on Type and Persistence of Chlorine and Iodine Residuals.

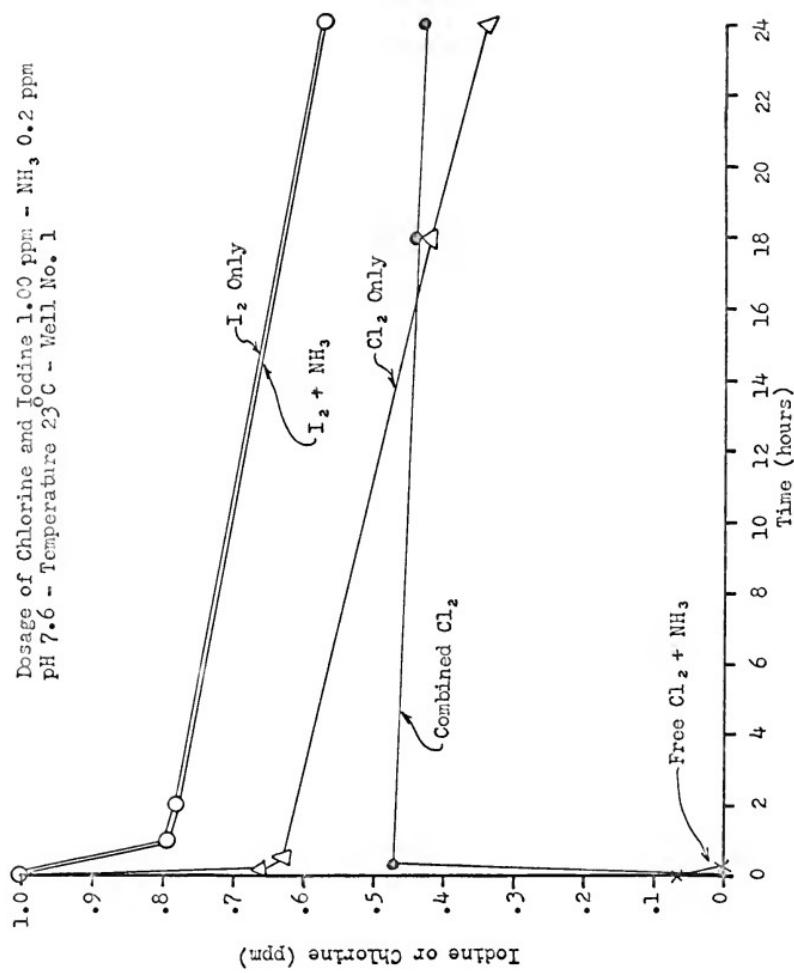


Fig. 55 - Effect of Added  $\text{NH}_3$  on Type and Persistence of Chlorine and Iodine Residuals.

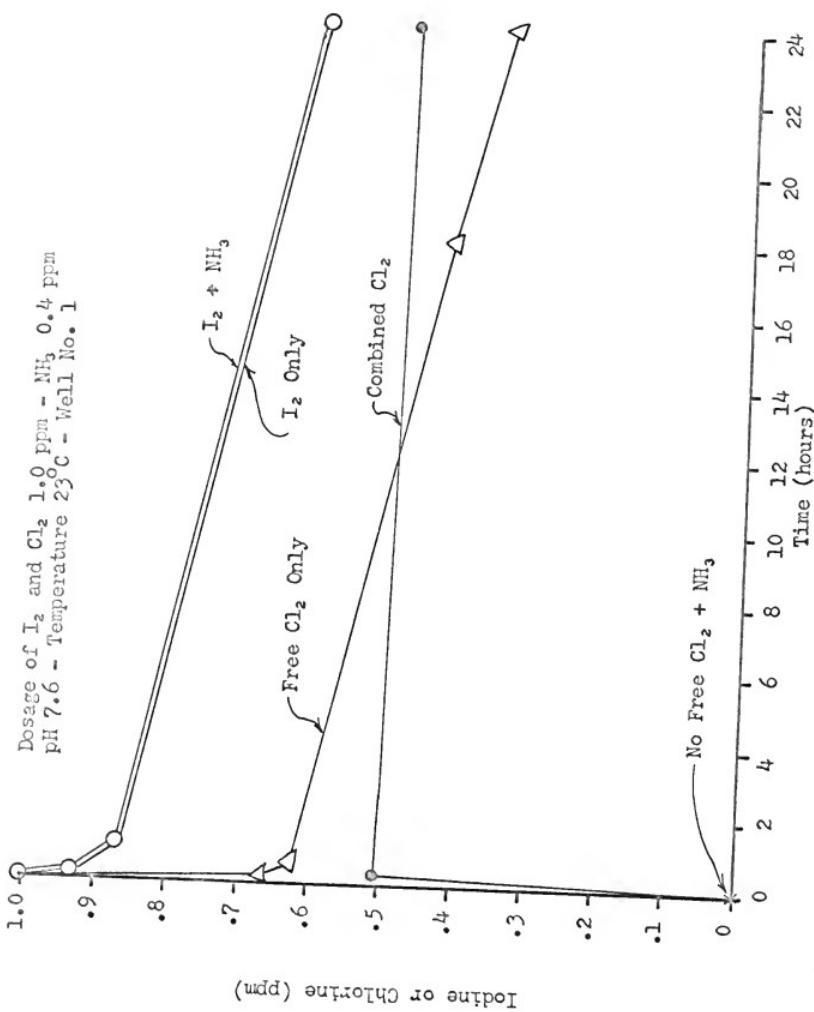


Fig. 56 - Effect of Added  $NH_3$  on Type and Persistence of  $Cl_2$  and  $I_2$  Residuals.

Concentrations of only 0.2 parts per million ammonia completely removed the 1.0 parts per million free available chlorine in less than 15 minutes, leaving ineffective chloramine compounds in the solution. Concentrations of 0.5 parts per million or more of NH<sub>3</sub> are frequently encountered in swimming pools. Mills<sup>42</sup> reported that analyses of several pools in Midland, Michigan, during the summer of 1964, showed ammonia levels as high as 1.6 parts per million ammonia. This instability of chlorine in the presence of ammonia and organic compounds is a distinct disadvantage in water disinfection, whereas the failure of iodine to react with these compounds is a valuable asset. Table 33 (after Mills) illustrates the tremendous increase in time required by chlorine to affect 99.9% kill of E. coli in the presence of ammonia.

Table 33  
Effect of Ammonia on Rate of Kill

Chlorine (ppm)	Ammonia (ppm)	Time for 99.9% Kill (sec.) E. coli
0.25	0	0 - 15
	0.1	180
	1.0	1200
2.0	0	0 - 15
	10.0	3600

Mills states that much of the published literature is in disagreement on the relative activity of chlorine and iodine. But there is little question that due to the larger detrimental effects of ammonia, pH, and sunlight, chlorine in most practical cases is less effective.

Effect of Added Raw Sewage on the Halogen Demand of  
Lowell Well Water

General Discussion

Many of our untreated water supplies are approaching the condition of open sewers and our water treatment procedures are severely tested each day in many large cities. This pollutional load is expected to increase before it decreases. In September 1964, the Water Pollution Control Federation reported in "Highlights"<sup>53</sup> that of our 190 million people, 118 million are served by sewers. Of this 118 million served by sewers, only 57% are served by secondary sewage treatment. Untreated and treated sewage and industrial wastes are now commonly present in many public water supplies. The Public Health Activities Committee of the Sanitary Engineering Division of the American Society of Civil Engineers reported in 1961<sup>54</sup> that "complete control of the hepatitis virus and probably other infectious agents in drinking water depends almost entirely on the disinfectant, as the virus is not eliminated or inactivated by coagulation, settling and filtration." Adequate water disinfection now requires that the disinfectant be capable of acting in the presence of gross sewage pollution. Therefore, it

appeared necessary to investigate the stability of iodine residuals in the presence of raw domestic sewage and to compare the stability of these residuals with the stability of chlorine residuals under the same conditions.

Raw domestic sewage contains many different compounds in small quantities and each compound may or may not exert a halogen demand. Table 34 presents the common constituents in human feces and Table 35 presents like data for human urine. The concentrations of these materials may vary from one sewage to another, and from day to day, but they are approximately the same. Industrial wastes may contain many exotic chemicals.

#### Experimental Techniques

##### Reagents

The reagents used are listed as follows:

1. Standard chlorine solution.
2. Standard iodine solution.
3. Standard phenolarseneoxide solution.
4. Buffer pH 4.0.
5. Buffer pH 7.0.

Raw University of Florida sewage was obtained from the comminuter at the sewage treatment plant. Raw Lowell sewage was obtained at a point just prior to the bar screen at the sewage treatment plant for the Women's Prison. The University of Florida sewage is primarily domestic sewage with trace quantities of many different compounds from the laboratories. Lowell sewage is normal domestic sewage.

Table 34  
Typical Constituents of Human Feces

---

Stercobilin	Cellulose
Urobilin	Nitrogen
Indole	Amylase
Skatole	Trypsin
Hydrogen Sulfide	Nucleases
Methyl Mercaptan	Maltase
Organic Acids	Sucrase
Calcium Phosphate	Lipase
Calcium Oxalate	Lysozyme
Iron Phosphate	Neutral Fats
Magnesium	Fatty Acids
Potassium	Soaps
Sodium	Sterols
Ammonia	Others
Bacteria	Virus

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Table 35  
Typical Constituents of Human Urine

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Urea	Aromatic Hydroxy Acids
Creatinine	Ketone Bodies
Uric Acid	Sulfur Compounds
Acid Phosphate	Phosphates
Proteins	Bacteria
Ammonia	Chlorides
Amino Acids	Sodium
Oxalic Acids	Potassium
Glucuronic Acid	Calcium
Benzoylglycine	Magnesium
Citric Acid	Glucose
Lactic Acid	Others
Fatty Acids	Virus

---

Procedure

Various quantities of raw fresh domestic sewage were added to two liter samples of Lowell water in brown glass acid washed bottles and the pH and temperature noted. The sewage was never more than one day old and each comparison between chlorine and iodine was run on the same sewage and with the same concentrations of sewage and each halogen. Immediately after the halogens were added the test was begun. Two hundred milliliter samples were withdrawn and halogen residuals measured at predetermined

time intervals. Both free available chlorine residuals and combined available chlorine residuals were determined. The free chlorine residuals were determined at pH 7.0 and the combined residuals were determined at pH 4.0 in the presence of excess potassium iodide. These procedures are outlined in STANDARD METHODS.

Discussion of Results

Figures 57 through 62 and Tables 36 and 37 illustrate the effect of sewage pollution on the iodine and chlorine demand of a water. Figure 57 shows the effect of increasing concentrations of sewage on iodine demand. It is seen from this figure that iodine residuals are not greatly affected by the presence of organic pollution. Increasing the sewage concentration from 0.5% by volume to 2.5% by volume, a five-fold increase, increased the 24 hour iodine demand by only 0.6 parts per million.

Figure 58 illustrates the difference between the iodine demand of a water and the chlorine demand of the same water in the presence of 0.5% by volume of raw domestic sewage and the combined chlorine formed under these conditions. The 24 hour chlorine demand is 0.54 parts per million greater than the 24 hour iodine demand. This difference is over 20% of the initial dosage.

Figures 59-through 62 demonstrate how much more rapidly chlorine residuals are depleted by sewage pollution than are iodine residuals. Table 36 presents these data. It is easy to see from these data that the greater the pollutional load, the greater will be the difference between the chlorine demand and the iodine demand. Consider the 30 minute

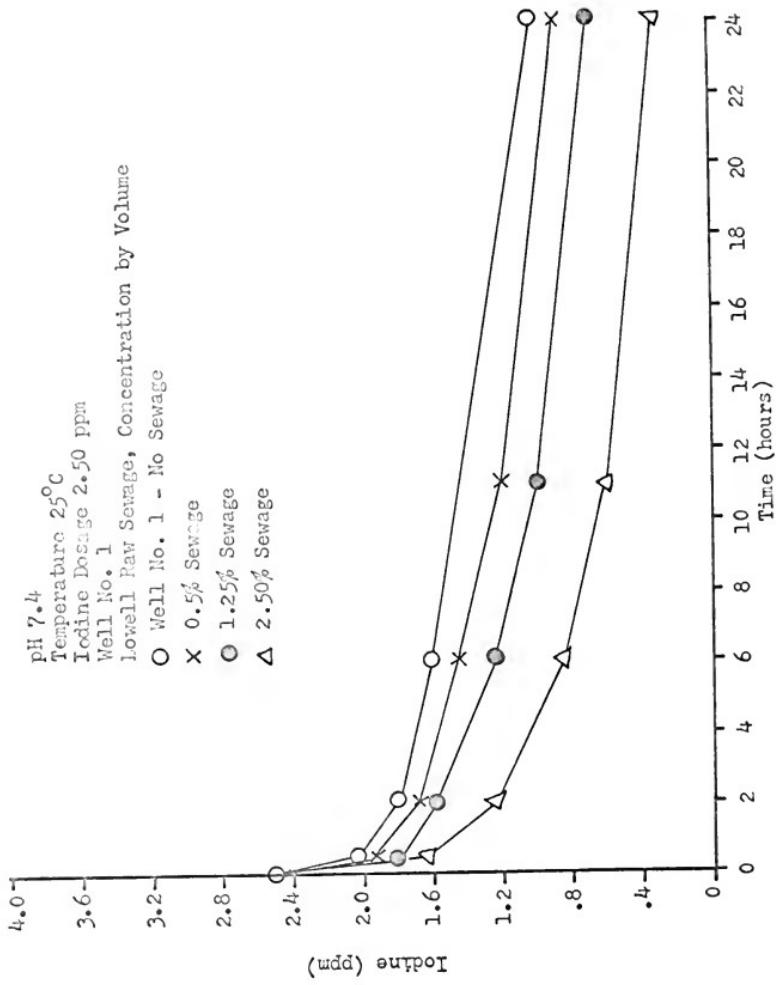


Fig. 57 - Effect of Domestic Sewage on the Persistence of Iodine Residuals.

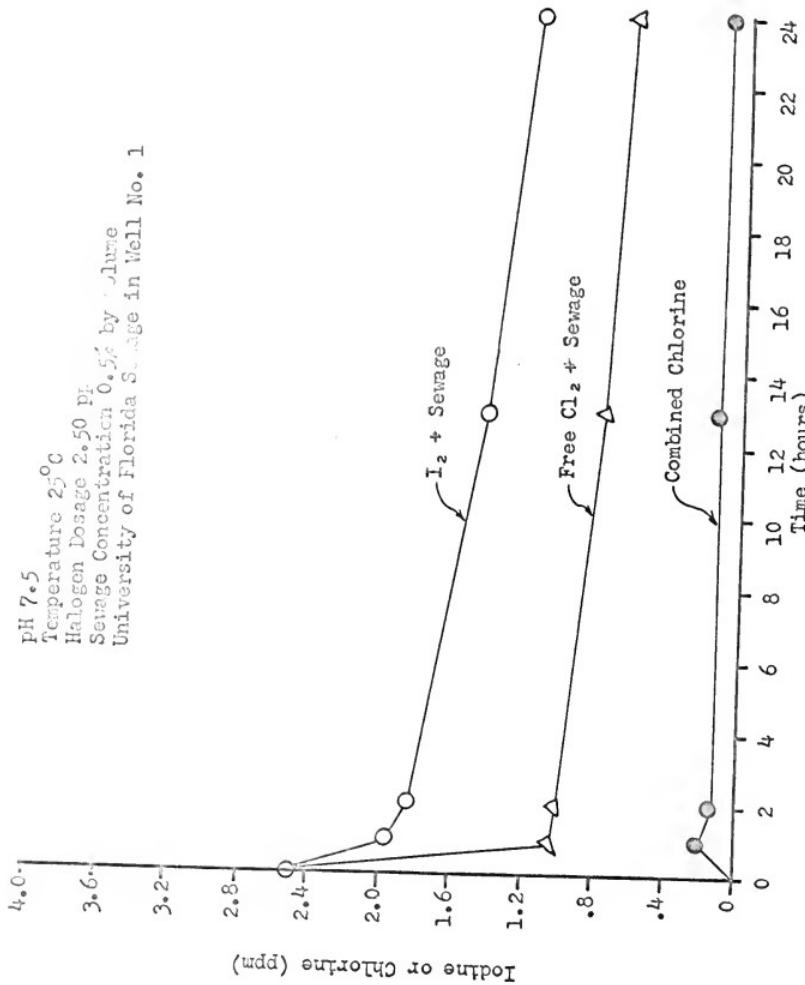


Fig. 58 - Effect of Domestic Sewage on the Persistence of Chlorine and Iodine Residuals.

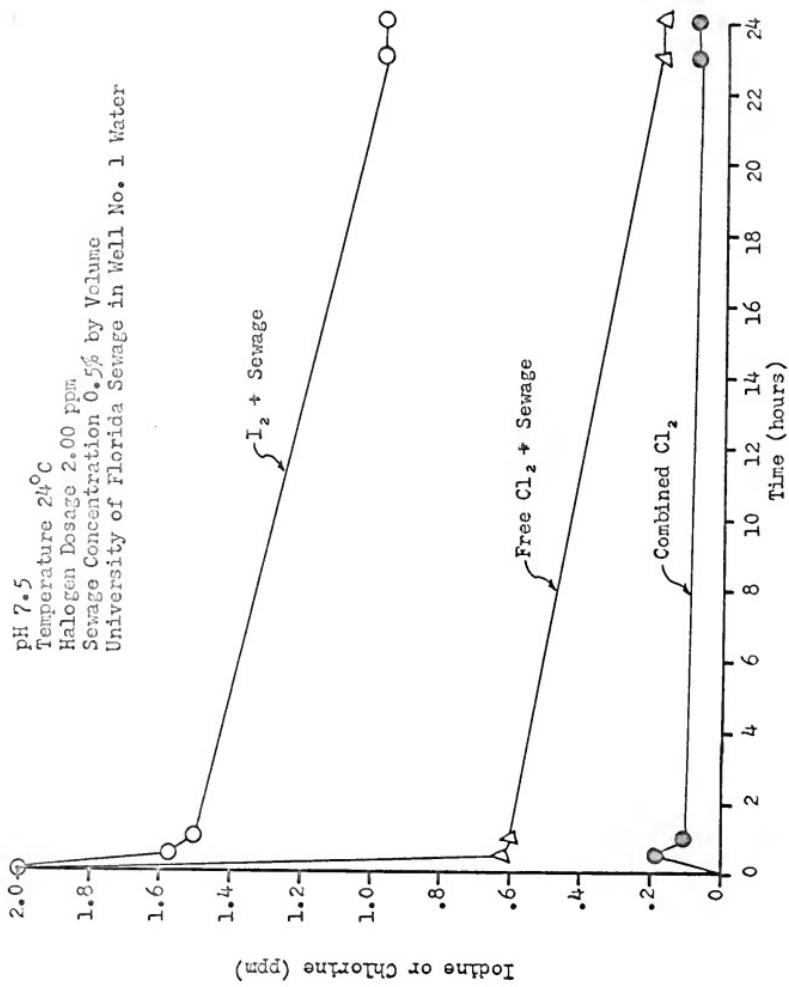


Fig. 59 - Effect of Domestic Sewage on the Persistence of Chlorine and Iodine Residuals.

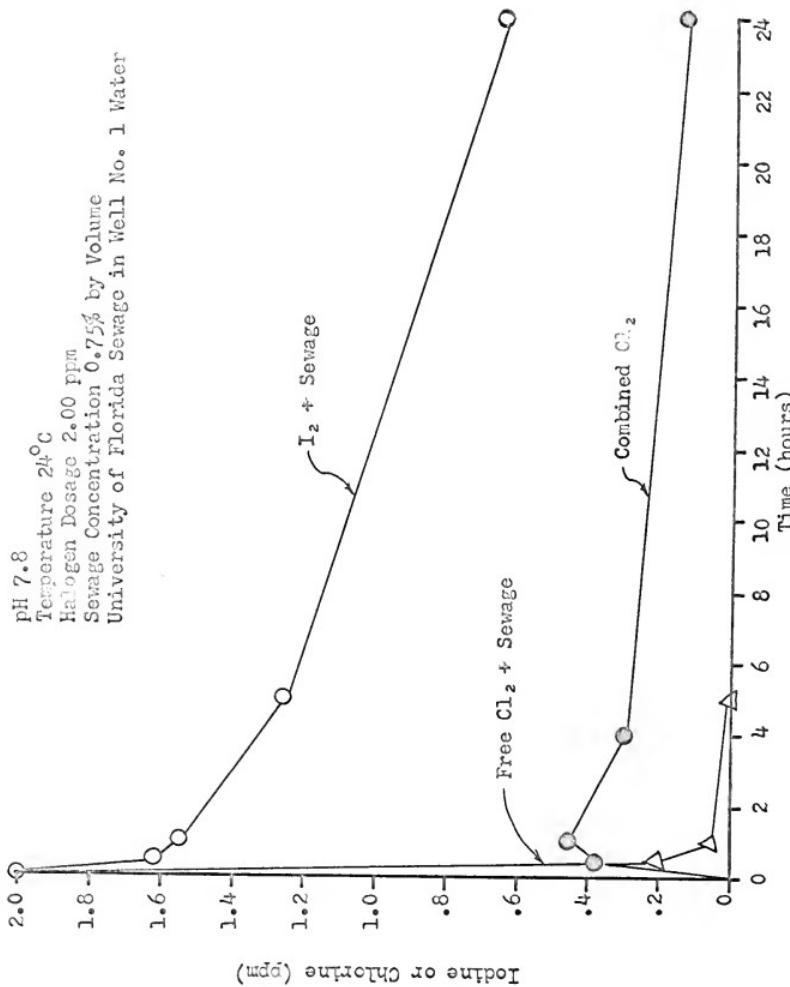


Fig. 60 - Effect of Domestic Sewage on the Persistence of Chlorine and Iodine Residuals.

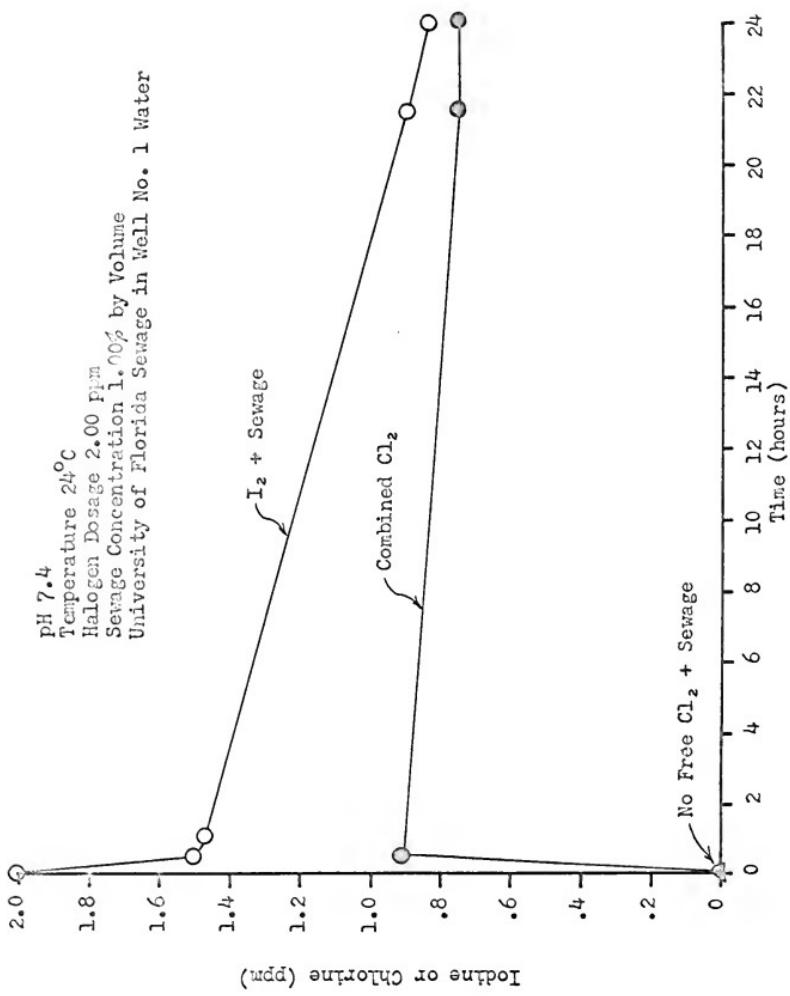


Fig. 61 - Effect of Domestic Sewage on the Persistence of Chlorine and Iodine Residuals.

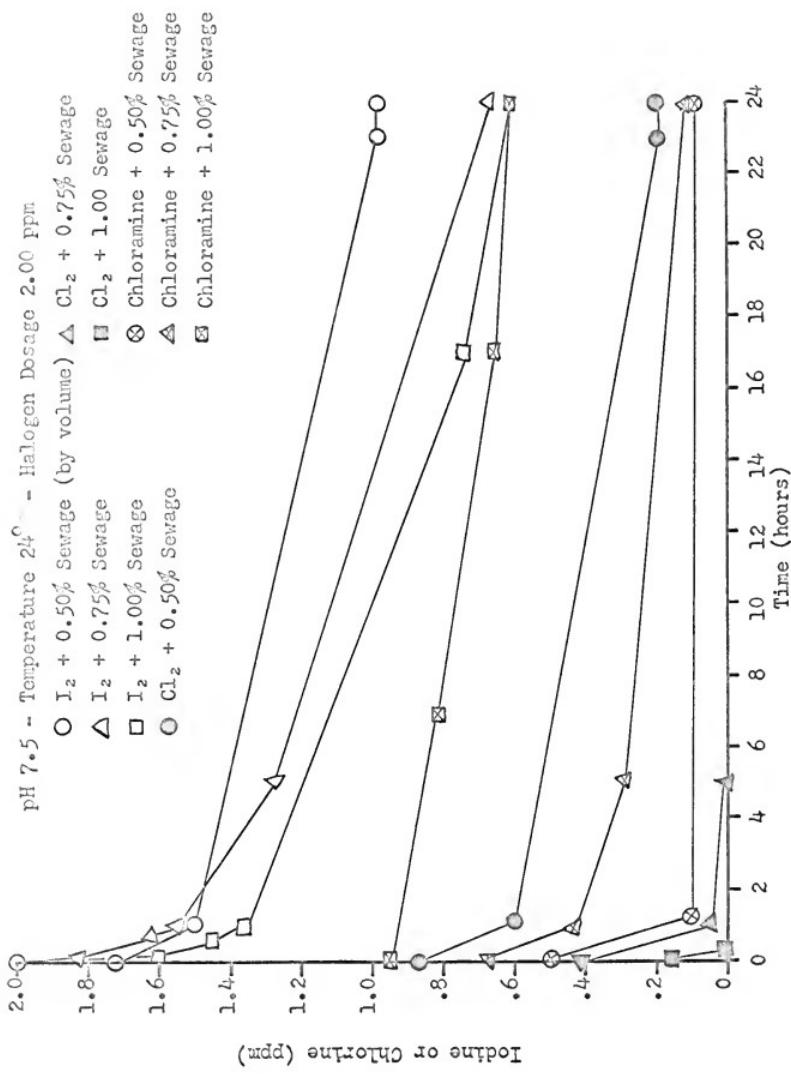


Fig. 62 - Effect of Domestic Sewage on the Persistence of Iodine and Chlorine Residuals.

Table 36

Effect of Sewage on Chlorine and Iodine Demand

Sewage Concentration Percent by Volume	Halogen Dosage ppm	Temperature °C	pH	30 Minute Demand I <sub>2</sub> ppm	Cl <sub>2</sub> ppm	1 Hour Demand I <sub>2</sub> ppm	Cl <sub>2</sub> ppm	24 Hour Demand I <sub>2</sub> ppm	Cl <sub>2</sub> ppm
0.50	2.0	24	7.5	.43	1.39	.50	1.41	1.03	1.82
0.75	2.0	24	7.8	.39	1.80	.46	1.95	1.36	2.00*
1.00	2.0	24	7.4	.50	2.00+**	.53	2.00+**	1.17	2.00+**

\* No free chlorine at five hours.

\*\* No free chlorine at 30 minutes.

Table 37

Effect of Sewage Concentration on Iodine Demand

Sewage Concentration Percent by Volume	I <sub>2</sub> Dosage ppm	Temper- ature °C	pH	30 Minute Demand ppm	1 Hour Demand ppm	24 Hour Demand ppm
0	2.5	25	7.4	0.48	0.70	1.50
0.5	2.5	25	7.4	0.58	0.82	1.60
1.25	2.5	25	7.4	0.70	0.92	1.82
2.50	2.5	25	7.4	0.86	1.28	2.20

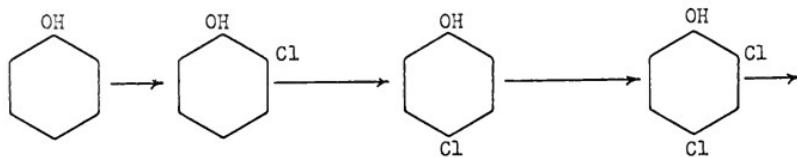
demand for both halogens. The 30 minute iodine demand is hardly affected by changing the sewage concentration from 0.5% by volume to 1.00%. It increases from 0.43 parts per million at the lower sewage concentration to 0.50 parts per million at the higher sewage concentration. This same increase in sewage concentration increases the 30 minute chlorine demand from 1.39 parts per million at the lower sewage concentration to over 2.00 parts per million at the high concentration. This means that in practice a water containing this much sewage would completely destroy 2.00 parts per million free chlorine in less than 30 minutes leaving only ineffective combined available chlorine in the water, whereas, if iodine was used for the disinfectant there would be available 1.50 parts per million iodine, 75% of the initial dosage, to continue disinfection. Certainly, some of the two parts per million of free available chlorine resulted in bacterial destruction, but most of the free available chlorine was converted into chloramines, as evidenced by the 0.90 parts per million combined available chlorine after only 30 minutes contact time. Ammonia in the sewage probably accounted for most of this rapid disappearance of free available chlorine, whereas ammonia has little or no effect on iodine in dilute aqueous solution. Hence, the iodine demand was only slightly affected by increasing the sewage concentration.

### The Effect of Phenol in Iodine Disinfection

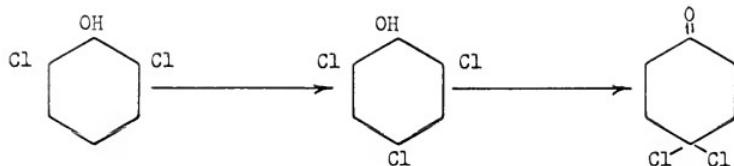
#### General Discussion

The term phenol is a collective term in water and waste water treatment, which includes all of the hydroxy derivatives of benzene, or its condensed nuclei that may be determined by the methods outlined in STANDARD METHODS.<sup>49</sup> Minute concentrations of phenol in waters that contain chlorine cause severe taste and odor problems resulting from the chlorination of the phenol or phenolic compounds. The United States Public Health Service in 1962<sup>46</sup> reaffirmed the upper limit of 0.001 mg/l (1 part per billion) phenol in drinking water. Accordingly, it was thought advisable to investigate the possibility that iodine might produce objectionable tastes or odors in phenol-bearing waters.

Burtschell and others<sup>55</sup> found that the chlorination of phenol proceeds by the stepwise substitution of chlorine in the 2, 4 and 6 positions of the aromatic ring to form strong-tasting intermediate species and finally non-tasting products. They listed these compounds in the order of their formation and determined that 2,6-dichlorophenol, 2,4-dichlorophenol and 2-chlorophenol are the taste and odor producing species. The compounds are formed as shown below:



phenol      2-chlorophenol      4-chlorophenol      2,4-dichlorophenol



2,6-dichlorophenol

2,4,6-trichlorophenol

4,4-dichloroquinone

Lee and Morris<sup>56</sup> studied the kinetics of the chlorination of phenol and chlorophenolic compounds. Their work agreed with the work of Burtschell and previous investigators. They demonstrated that the water works practice of superchlorination followed by dechlorination has great merit in terms of elimination of "chlorophenolic" tastes and odors in water supplies.

Hunter and Budrow<sup>57</sup> studied the iodination of phenol and phenolic compounds and found that pure phenol does not react with iodine to any appreciable extent. They were able, however, to iodinate sodium phenolate under anhydrous conditions to form orthoiodophenol, di-iodophenol and tri-iodophenol. Other studies have shown that iodine is relatively inactive in direct substitutions. Carboxylic acids are in general quite stable towards it even at fairly high temperatures. No reaction was found when acetic acid was heated with iodine at 100°C.

Experimental Techniques

Reagents

A stock solution of pure phenol was prepared in double demineralized water and standardized by the aminoantipyrine method as given in STANDARD METHODS. This solution was adjusted to a concentration of 1000 micrograms phenol per liter.

A standard iodine solution of 1000 milligrams per liter was prepared according to STANDARD METHODS and stored in a brown glass bottle.

All pH measurements were made on a Beckman Model G pH meter.

All iodine residuals were determined by amperometric titration with a Wallace and Tiernan amperometric titrator.

These studies were carried out with the water from Lowell Well No. 3.

Procedure

Predetermined quantities of phenol were added to two liter samples of Lowell water in brown glass bottles. The pH and temperature were determined and one part per million of iodine was added. Iodine residuals were determined at predetermined intervals and all samples were checked for the possible presence of odors and tastes. Each test was run in duplicate and a blank sample containing only iodine was run for the demand comparison. Table 38 presents the data for the 30 minute and six hour iodine demands both for the control and the phenol-containing samples and the results of the taste and odor tests. Figures 63 and 64 are typical demand curves for the phenol and control samples.

Table 38

## The Effect of Phenol on Taste or Odor and Iodine Demand

- 163 -

Phenol ppb	Iodine ppm	pH	Temperature °C	$I_2$ Consumed Control ppm	$I_2$ Consumer After 30 min. Sample ppm	$I_2$ Consumer After 6 hrs. Control ppm	$I_2$ Consumer After 6 hrs. Sample ppm	Tastes or Odors Present after 24 hrs.
0.1	1.00	7.6	24	0.07	0.07	0.25	0.18	None
0.2	1.00	7.6	24	0.14	0.11	0.25	0.25	n
0.5	1.00	7.6	24	0.11	0.11	0.18	0.18	n
1.0	1.00	7.6	24	0.07	0.07	--	--	n
2.0	1.00	7.6	24	0.02	0.02	0.07	0.07	n
5.0	1.00	7.6	24	0.04	0.04	0.14	0.14	n
10.	1.00	7.6	24	0.07	0.07	--	--	n
15.	1.00	7.6	24	0.07	0.07	0.22	0.22	n
30	1.00	7.6	24	0.07	0.07	0.14	0.14	n
60	1.00	7.6	24	0.11	0.14	0.29	0.25	n

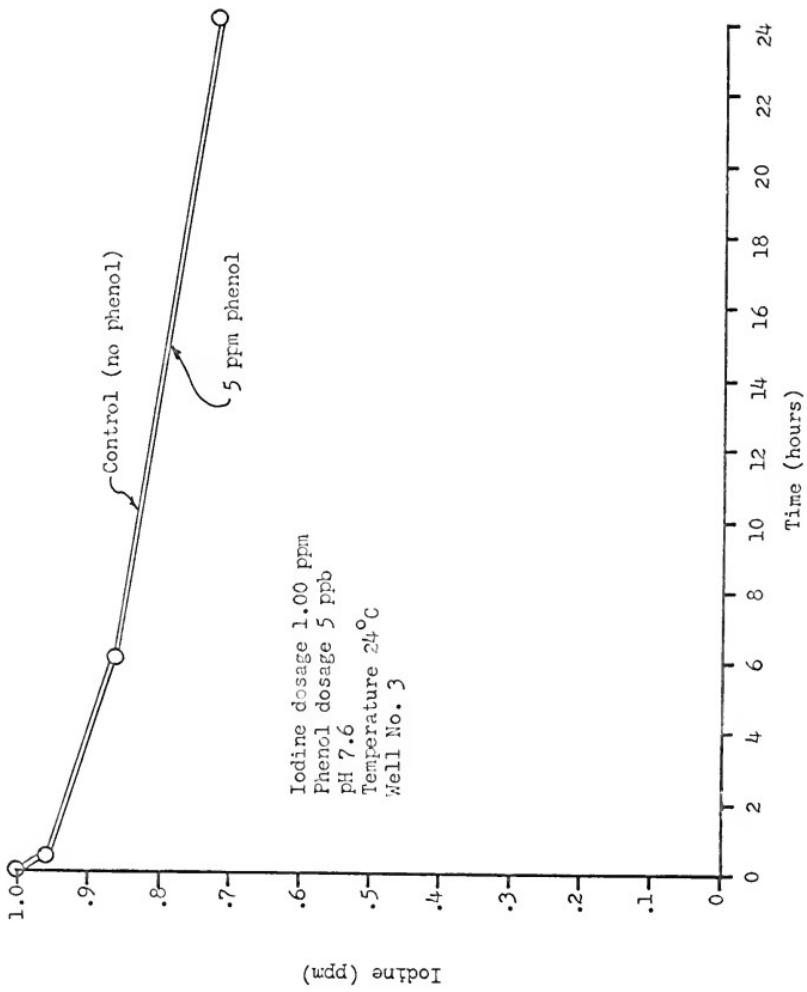


Fig. 63 - Effect of Phenol on Iodine Demand.

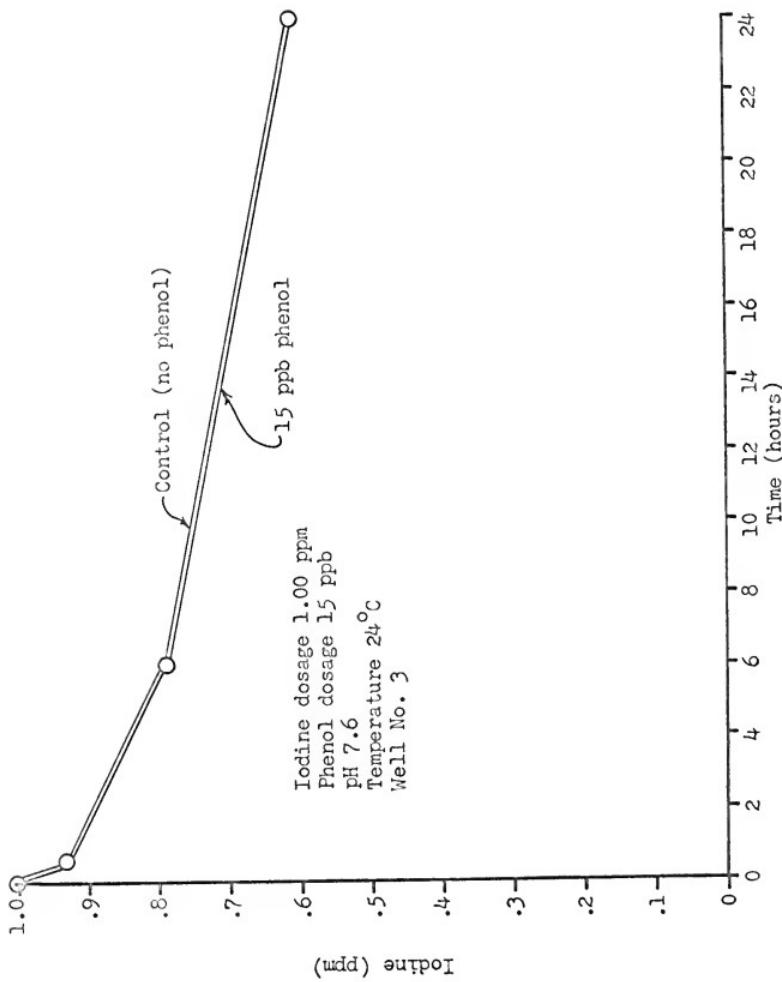


Fig. 64 - Effect of Phenol on Iodine Demand.

#### Discussion of Results

None of these tests indicated any reaction between phenol and iodine in 24 hours, either by increase in iodine-demand or by the production of tastes and odors. Other tests were run over periods of several days in which water samples were dosed with iodine and phenol and left standing in brown bottles for up to seven days. Sixty parts per billion of phenol did not produce any tastes or odors after seven days contact with iodine. These tests indicate that iodine in disinfectant concentrations does not react with phenols in concentration far in excess of those now recommended by the United States Public Health Service. Iodine can therefore be used to disinfect waters which cannot be chlorinated because of their phenol content.

#### Effect of Iodine on Copper

##### Introduction

The only indication of any difference in taste between the original water and the iodinated water at Lowell came from comments of a few individuals to the effect that the water possessed a metallic taste at the refrigerated drinking fountains. This "metallic taste" was never noted by the author, but it appeared worthy of investigation. These drinking fountains employ copper coils in which the water is cooled before it is consumed, so copper became the object of investigation. A large percentage of all home water services are made of copper, hence it is important to know whether iodine and copper are compatible under the conditions of water disinfection and distribution as practiced at the present time. Iodine and iodide in high concentrations react readily

with copper to form a black copper iodide coating. This same type reaction occurs between iodine and silver to form a coating of silver iodide on silver metal. This reaction occurs readily in iodine disinfected swimming pools at the low iodine concentrations which approximate drinking water disinfection. The author has demonstrated this by placing silver coins in an iodine disinfected pool and some bathers have noted a discoloration of silver jewelry in such water. Hence, a reaction between copper metal and iodine in low concentrations to form copper iodide would not be unexpected.

Experimental Techniques

Procedure

Three types of laboratory tests were carried out to examine the effect of iodine on copper in dilute aqueous solution. One of these consisted of immersing a piece of copper tubing in strong iodine solution (1000 ppm) and in strong iodide solution (10,000 ppm). Both of these experiments resulted in the formation of a black coating on the metal and severe attack with pitting and flaking of the copper metal. A second test consisted of immersing pieces of copper tubing in low concentrations of iodide (1-20 ppm) with no iodine present. In a third test, the iodine demand of a sample of water exposed to copper for various periods of time up to 24 hours was compared to the iodine demand of the same water unexposed to copper. A fourth test consisted of placing copper metal in contact with iodine vapor provided by iodine crystals in stoppered glass bottles.

The procedure in test one is self explanatory. In test two 20

glass bottles were filled with water from Lowell Well No. 1 and iodide ion added to provide concentrations from 1-20 ppm. A one inch piece of polished copper tubing was placed in each bottle and the bottles were placed on the laboratory shelf. After each day for ten days the pieces of copper tubing were examined for any visible signs of deterioration. Each piece of copper had 2.02 square inches of surface area exposed to the iodide. In the third test various lengths of polished copper tubing, one-fourth inch in diameter, were placed in brown glass bottles which contained two liters of water from Lowell Well No. 1 with an iodine concentration of 1.00 parts per million. The iodine demand of the samples containing the copper tubing were compared with the iodine demand of the same water without the polished copper tubing. Table 39 and Figures 65 through 69 present these data.

#### Discussion

Copper metal reacts very readily with iodine vapor, iodine crystals and high concentrations of aqueous iodine and aqueous iodide. Either the aqueous iodide or iodine will attack the metal rapidly when in high concentrations. In waters containing the very low iodine residuals necessary for disinfection, the rate is negligible. Figures 65 through 69 illustrate the small increase in 24 hour iodine demand due to the presence of metallic copper.

Table 39  
Iodine Demand of Water Exposed to Metallic Copper

Copper Tubing (inches)	$I_2$ Present ppm	pH	Temper- ature °C	1 Hour Demand		6 Hour Demand		24 Hour Demand	
				Control ppm	Test ppm	Control ppm	Test ppm	Control ppm	Test ppm
1	1.00	7.5	23.5	0.07	0.07	0.20	0.23	0.39	0.57
2	1.00	7.5	23.5	0.07	0.07	0.14	0.25	0.39	0.57
3	1.00	7.4	23.5	0.07	0.14	0.19	0.34	0.39	0.75
4	1.00	7.4	23.5	0.13	0.13	0.18	0.30	0.39	0.82
5	1.00	7.5	23.5	0.11	0.14	0.18	0.43	0.36	1.00

Note: The copper source was one-fourth inch in diameter polished tubing.

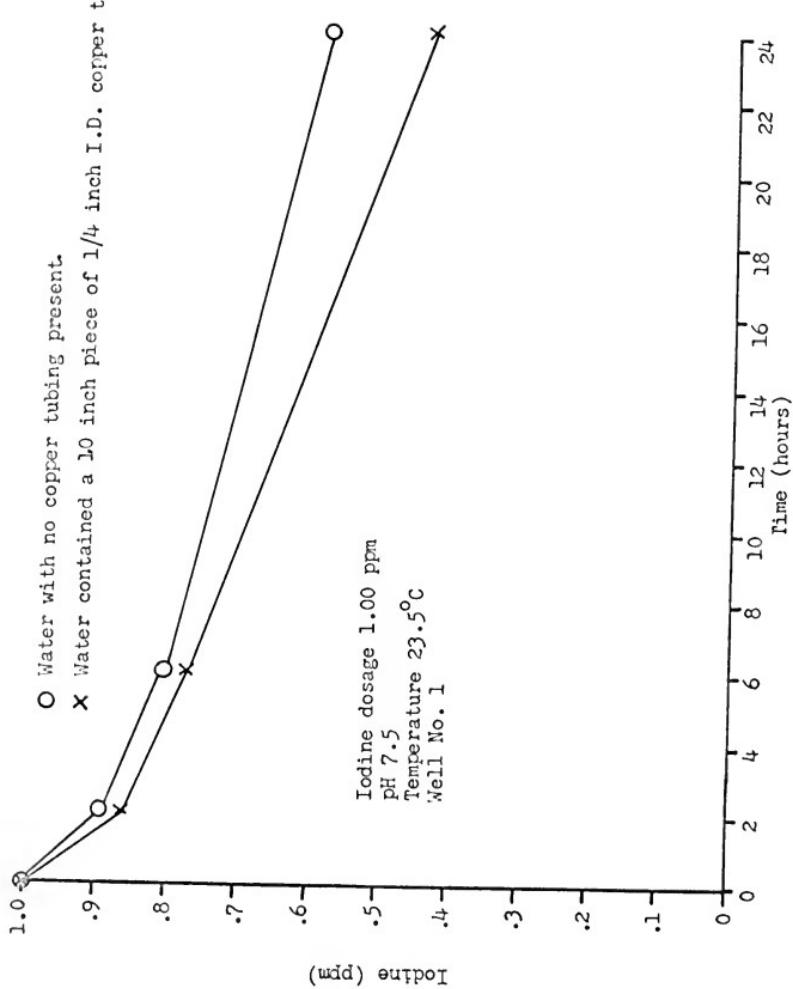


Fig. 65 - Iodine Demand of Water Exposed to Metallic Copper.

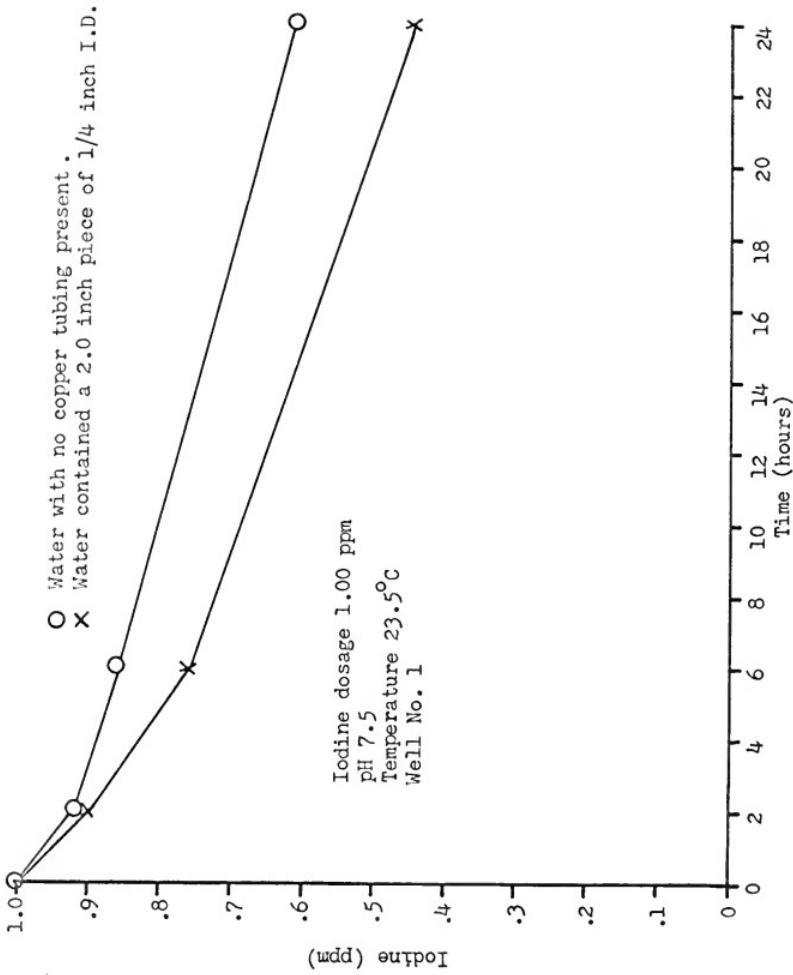


FIG. 66 - Iodine Demand of Water Exposed to Metallic Copper.

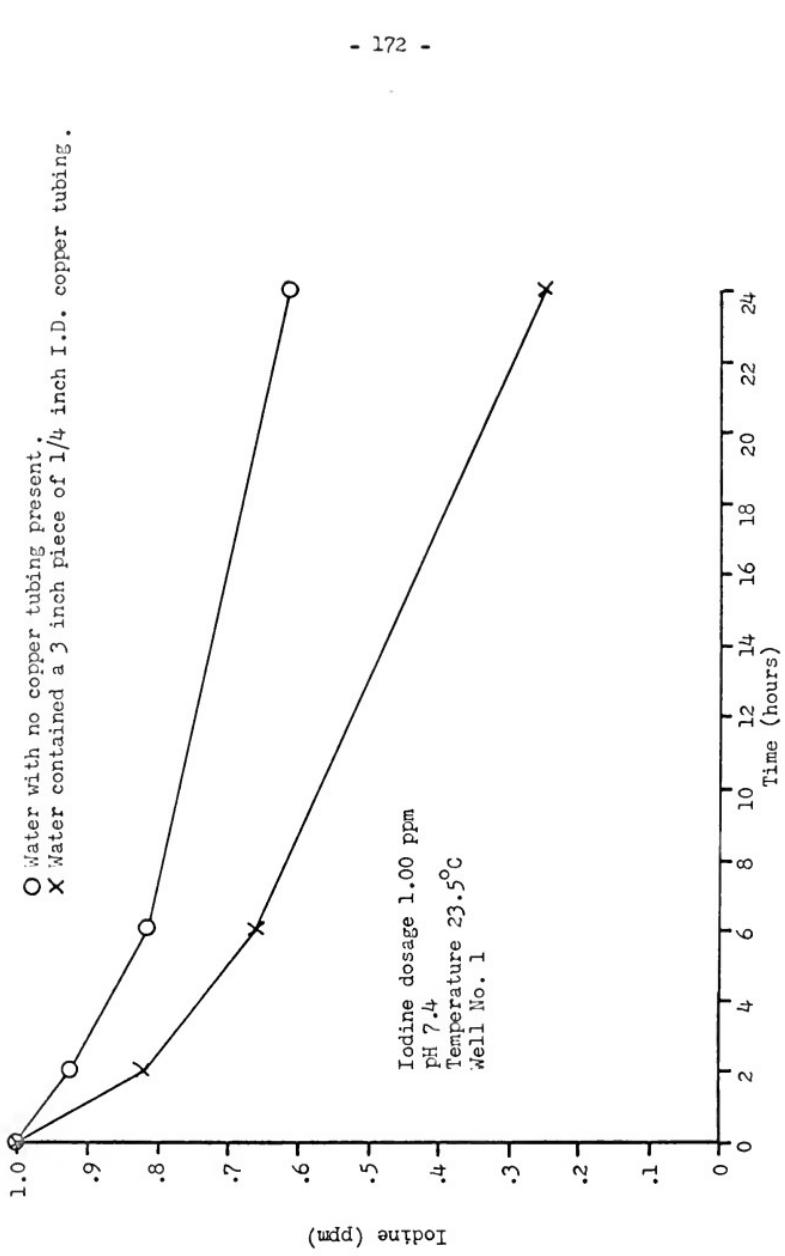


Fig. 67 - Iodine Demand of Water Exposed to Metallic Copper.

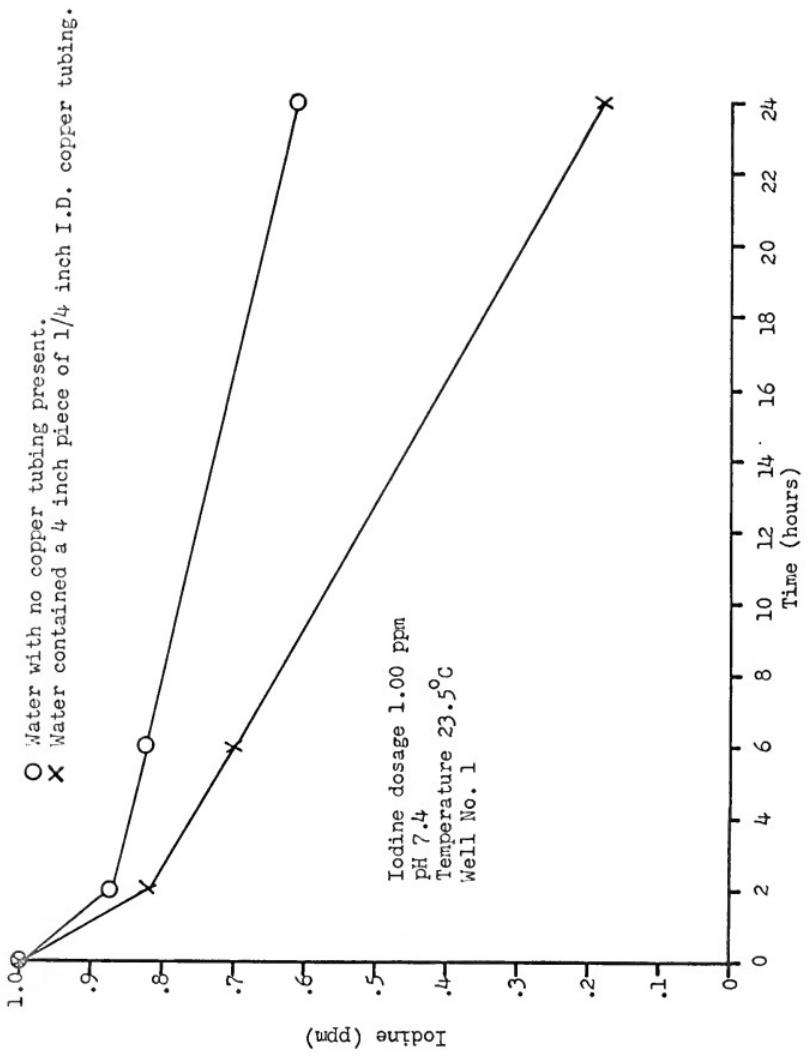


Fig. 68 - Iodine Demand of Water Exposed to Metallic Copper.

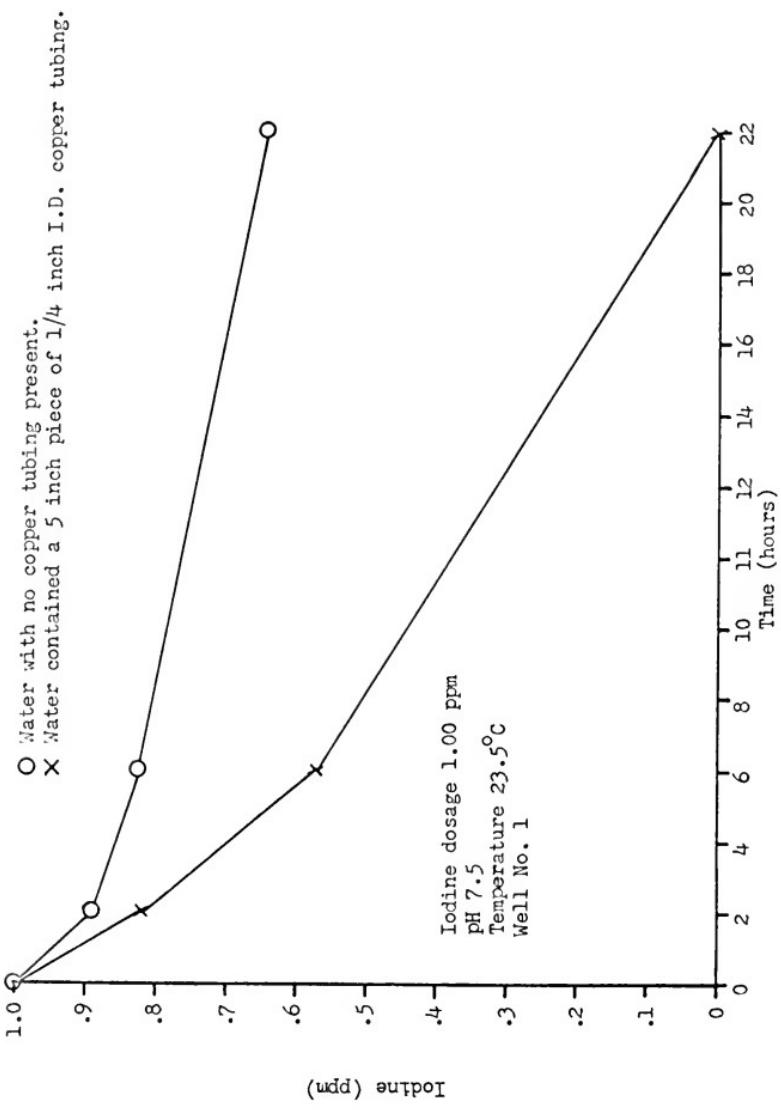


Fig. 69 - Iodine Demand of Water Exposed to Metallic Copper.

### Effect of Iodine on Materials of Construction

#### Introduction

In order to select materials to be used for iodine feeding and pumping equipment, it was necessary to consider the problem of corrosion. A search of the literature revealed scant quantitative information about the iodine-resistance of various materials of construction. Iodine reacts with every known element to some extent, so it would be expected to react with many materials of construction, and this is the case. Table 40 lists several common materials of construction which were reported to be iodine-resistant under suitable conditions in the Encyclopedia of Chemical Technology.<sup>12</sup> Several of the cheapest and most readily available of these materials were selected for this study.

Table 40

Materials that are Resistant to Iodine Under  
Suitable Conditions<sup>12</sup>

---

High-silicon iron	Chemical stoneware
Stellite No. 6	Enameled steel
Hastelloy C	Acid-proof brick
Stainless steel type 304	Carbon
Stainless steel type 309	Graphite
Stainless steel type 316	Wood
Stainless steel type 317	Teflon
Medium carbon steel (0.21% C)	Saran
Hastelloy B	Glass
Molybdenum	Hard lead
Lead-coated steel	

---

Procedure

Several of the materials in Table 40 plus many more were subjected to some simple laboratory tests. These tests consisted of placing the material under study in contact with various concentrations of iodine in aqueous solution and in contact with the element itself in closed glass jars at room temperature. On the basis of these tests, certain of these same materials were used to fabricate the iodination assembly at Lowell. The results from the laboratory tests are shown in Table 41 and the results from the use of the materials at Lowell are presented in the following pages.

Immersion Test Procedures

Materials under study were placed in contact with iodine in different forms and under different conditions at room temperature in glass bottles. The materials were placed in aqueous iodine solutions alone and in iodide solution. Iodide solutions of 50,000 parts per million were used for the iodide test.

Discussion of Immersion Test Results

Table 41 lists materials which have been found satisfactory for use in iodine technology. Several of the more common chemical-resistant materials are not resistant to iodine. Rubber is a good example. It is very resistant to many chemicals, but it cannot be used to handle elemental iodine, iodine vapor or aqueous iodine. Rubber may be used for iodide solutions if they are iodine-free. Iodine causes rubber to crack, harden, and lose its useful properties.

Polyethylene is another commonly used resistant material which

Table 41

Common Construction Materials Resistant to Iodine

	Iodine Crystals	Iodine Vapor	Aqueous Iodine	Aqueous Iodide
Glass	+	+	+	+
Vitrified Clay	+	+	+	+
Plexiglass	+	+	+	+
Teflon	+	+	+	+
Saran	+	+	+	+
Penton	+	+	+	+
Polypropylene	+	+	+	+
Polyvinylchloride	+	+	+	+
Tygon Tubing	-	-	+	+
Fiberglass	-	-	+	+
Stainless Steel 305	-	-	+	+
Stainless Steel 316	-	-	+	+
Stainless Steel 347	-	-	+	+
Monel	-	-	+	+
Inconel	-	-	+	+
2-ton Epoxy Cement	-	-	+	+
Wood	+	+	+	+
Polyethylene	-	-	-	+
Rubber	-	-	-	+
Graphite	-	-	+	+

<sup>+</sup>Indicates the material which was not affected by the particular form of iodine noted during the period of exposure. (Two years).

<sup>-</sup>Indicates that the material was adversely affected by the form of iodine noted.

cannot be used to handle iodine solutions. It may be used to handle iodine-free iodide solutions. Iodine solutions penetrate the material.

Copper is not very resistant to concentrated iodine or iodide solutions. Concentrated iodide solutions cause a coating to be formed on the surface of the metal plus scaling and flaking of the metal into solution. The attack on copper by concentrated iodine solutions is rapid.

Aluminum has little resistance to iodine and hence cannot be used to handle iodine solutions. Additionally, many paints are discolored and spotted by iodine solutions.

#### Iodine-Resistance of Construction Materials at Lowell

##### Material: Hastelloy C

Use - All of the iodine feed pump plungers were composed of this material. The strength of the iodine solution in continuous contact with these plungers for over 20 months was 305 parts per million elemental iodine in aqueous solution with no iodides present.

##### Performance - Excellent.

Discussion - These pump plungers did not show any evidence of any effect from the iodine solution. One plunger was carefully inspected after 2000 hours of continuous pumping and showed no visible signs of any corrosion or any effect whatsoever from the saturated iodine solution. None of the pump plungers after 24 months of exposure to saturated aqueous iodine (305 parts per million) have shown any deterioration.

Material: Stainless Steel Type 304

Use - Stainless steel tubing type 304 was used to carry saturated aqueous iodine (305 parts per million) from the iodine saturator to the feed pump and on to the raw water.

Performance - Excellent.

Discussion - Stainless steel type 304 withstood saturated aqueous iodine solutions (305 parts per million) for over 20 months with no visible effect at a pressure of 60 pounds per square inch and a temperature of 21.5° C.

Material: Stainless Steel Type 347

Use - Stainless steel type 347 was used to carry saturated aqueous iodine (305 parts per million) from the iodine saturator to the feed pump.

Performance - Excellent.

Discussion - Stainless steel type 347 withstood saturated aqueous iodine solutions (305 parts per million) for over 22 months with no visible effect at a pressure of 60 pounds per square inch and temperature of 21.5° C.

Material: Stainless Steel Type 316

Use - All iodine feed pump heads were made of 316 stainless steel. All elbows, unions and other pipe fittings conveying saturated aqueous iodine were made of 316 stainless steel. Valve bodies and stems for those valves on the iodine feed lines were made of this same material.

Performance - Excellent.

Discussion - The 316 stainless steel pump heads, valve parts and fittings showed no visible deterioration after 22 months contact with saturated aqueous iodine (305 parts per million) at 60 pounds per square inch and 21.5°C.

Material: Inconel

Use - Inconel tubing was used to carry saturated aqueous iodine solution (305 parts per million) from the feed pumps to the raw water line.

Performance - Excellent.

Discussion - Inconel was also used to convey saturated iodine solution from the saturator to the raw water. No evidence of deterioration of any kind was visible.

Material: Graphite

Use - Graphite was the chief constituent in all the packing in the feed pumps.

Performance - Excellent.

Discussion - Two of the feed pumps developed slight leaks, after four months of use in the one case and six months in the other. These leaks were very minor, about 50 milliliters in 24 hours, but the packing was removed and examined for deterioration of any kind. The packing was in good condition, but it was replaced with new packing. This slight leak of about 50 milliliters per 24 hours has developed in two of the pumps, but it does not increase and could be easily corrected by installing a packing wash line. Packing which has been removed after months

of service has some iodine adsorbed on it, but the graphite packing has withstood any attack by the iodine. The packing in the pump at Station No. 2 has never been changed and has been in service for over 24 months, and does not leak.

Material: Glass

Use - The bottom of the saturators are composed of a one-fourth inch thick glass plate held in place by concrete and the iodine support bed is composed of glass beads and glass marbles.

Performance - Excellent.

Discussion - Glass is resistant to iodine in all forms. None of the glass used at Lowell showed any signs of damage. The glass beads did have iodine adsorbed on the surface.

Material: Saran

Use - A thin sheet of Saran served as a vapor seal for the saturators at Lowell and the laboratory saturators. Saran has served so well that the new steel saturators are lined with Saran throughout. One of these Saran-lined saturators has been in service for 11 months.

Performance - Excellent.

Discussion - Saran is one of the best iodine-resistant materials commercially available. It is resistant to all forms of iodine and is tasteless, odorless and nontoxic. It is readily available as a thin sheet, machined pipe fittings and Saran-lined steel pipe. Tanks and other containers can be lined with Saran in place. A double thickness layer of the household Saran-wrap has served as an effective vapor seal

for both laboratory saturators and the saturators in service at Lowell for over 22 months. Iodine is adsorbed on the surface and hence discolors the Saran, but there has been no change in the physical properties of the Saran in contact with the elemental iodine and iodine solution.

Material: Teflon

Use - Teflon valve seats were used in all the valves handling saturated iodine solution.

Performance - Excellent.

Discussion - Teflon is probably the most chemically resistant plastic material available at this time. It is expensive, but it is readily available in many forms. The Teflon valve seats at Lowell have resisted saturated aqueous iodine with no leakage and no signs of deterioration for over 24 months.

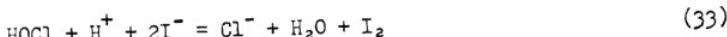
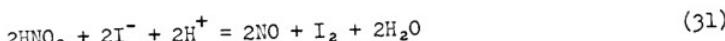
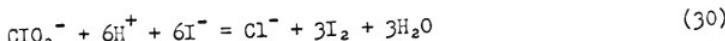
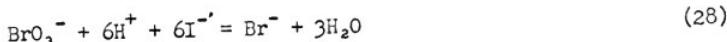
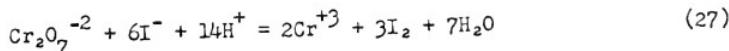
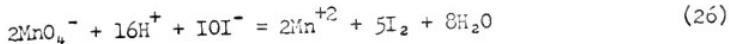
Reoxidation of the Iodide Ion

Introduction

Iodine is a weak oxidizing agent. The half-cell emf for the oxidation is -0.54 volts.



Many determinations in analytical chemistry are based upon the oxidation of iodide ion to elemental iodine under proper conditions. Several of the classical reactions are presented on the next page to indicate how widely this reaction is used.



Reaction 29 is the basis for the determination of iodate ion in acid solution and the last reaction is the one most used in swimming pool disinfection with iodine.

Iodine reacts with microorganisms and trace impurities in water and is reduced to iodide ion. This constitutes much of the so-called demand and it is a function of iodine concentration, time, temperature, pH and concentration of microorganisms and trace reducing agents in the water. Iodine is such a weak chemical that practically none of the iodine becomes bound to the other compounds in the water in such a way that it can no longer be reoxidized to elemental iodine. Black<sup>32</sup> has calculated that the iodide ion may be reused as much as 13 times in a swimming pool before being lost. This factor helps to explain the reduction in disinfection cost for a swimming pool when iodine is used in place of chlorine as the disinfectant. At Lowell, the difference

between the administered dose of elemental iodine and the iodine residual existing at the ends of the system is iodide ion. This means that effective disinfecting residuals can be maintained in major distribution systems by successive reoxidation of the iodide ion to elemental iodine. Figure 70 dramatically illustrates what takes place when iodine is added to a water containing a small residual concentration of monochloramine. Without the monochloramine the element exerts its disinfection action and a measurable iodine residual persists for only 17 hours. However, in the presence of 0.5 parts per million of monochloramine an effective residual is present in the water for more than 68 hours. The great importance of this unique property of iodine is that it should make it possible to maintain water of high quality for longer periods of time in distribution systems and thus assist in solving a problem which has never been satisfactorily solved by the water works industry. A study was initiated to find a cheap, nontoxic inorganic oxidizing agent suitable for this purpose, similar in action to monochloramine.

#### Experimental Technique

Reagents - all at identical concentrations of 1 mg/ml.

1. Standard sodium perborate tetrahydrate.
2. Standard sodium borate perhydrate.
3. Standard sodium, zinc and calcium peroxides.
4. Standard hydrogen peroxide.
5. Standard sodium persulfate
6. Standard potassium persulfate.
7. Standard potassium peroxyomonosulfate.

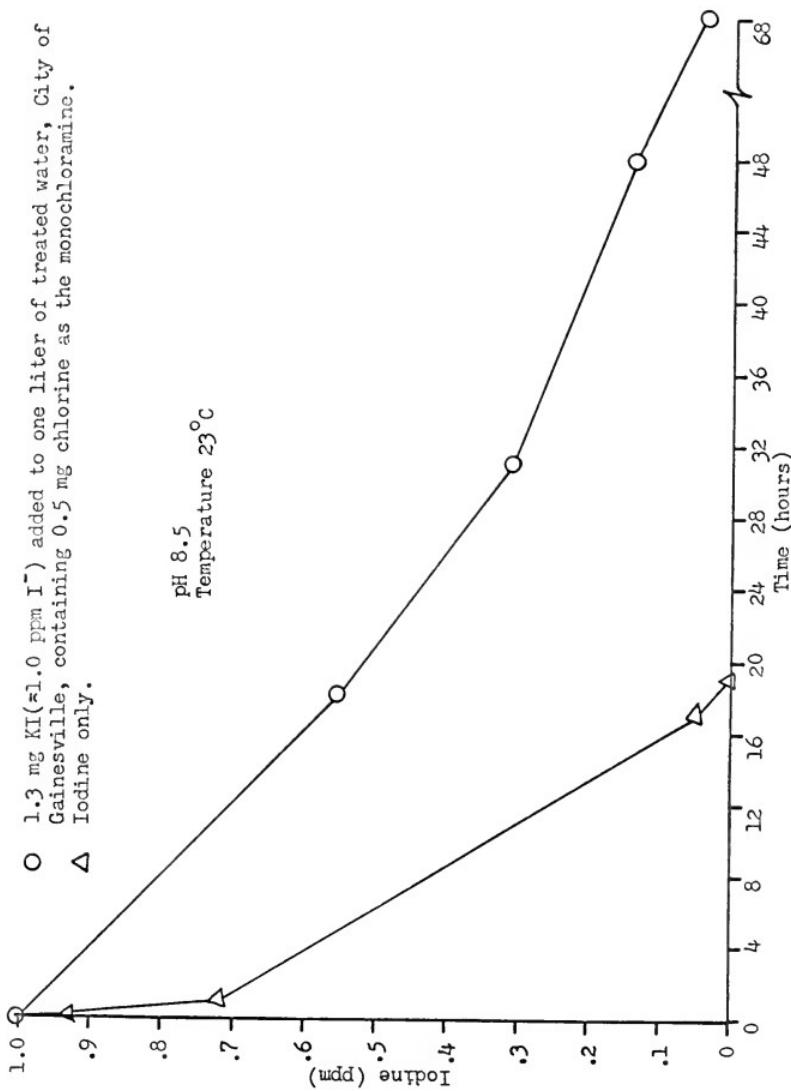


Fig. 70 - Effect of Monochloramine on Persistence of Iodine Residuals.

8. Standard potassium iodide.
9. Standard ammonium persulfate.
10. Standard sodium nitrate.
11. The Whittle test kit.

#### Procedure

Two hundred milliliter samples of demineralized water buffered to the desired pH and Lowell well water were placed in glass bottles, and quantities of iodide from 1-5 parts per million were placed in these samples. Varying quantities of the oxidant under study were added to these samples and the samples were tested for the presence of iodine at selected time intervals using the Whittle iodine test kit. It was hoped that an oxidant could be found that would yield iodine in from 12 to 24 hours in the range of from pH 7.0 to pH 9.5 at room temperatures, with concentrations of iodide and oxidant less than five parts per million. Concentrations of oxidants much higher than five parts per million were tried, and each oxidant was tried at lower pH values. Each test was conducted for a minimum of 48 hours. A Beckman Model G pH meter was used to determine pH. Table 42 lists the compounds tested and the results obtained.

#### Discussion

The object of this study was to find a cheap, nontoxic, inorganic oxidizing agent which would oxidize iodide ion to elemental iodine in dilute aqueous solution, and which would be completely compatible with iodine in the system. The ideal oxidant would convert the iodide ion to iodine as the reduction of iodine to iodide occurs. Only three oxidants

were found which would oxidize iodide ion to iodine under the test conditions. Of these three, monochloramine most nearly meets all of the requirements of the system. It is compatible with iodine and it oxidizes the iodide to iodine without converting the iodine to iodate. Chlorine and oxone will perform the oxidation of  $I^-$  to  $I_2$  rapidly, but they are not compatible with the iodine formed. Any excess of either of these compounds in the system converts the iodine to iodate, which is no longer useful in the disinfection process, and hence constitutes a loss of iodine.

All of the other compounds tested will oxidize  $I^-$  to  $I_2$  under proper conditions. Each performs the oxidation below pH 5.0. Most public water supplies have a pH above 7.0, so this eliminates their usefulness for this application. The possibility exists that a catalyst might cause these compounds to perform the oxidation under distribution system conditions, but this is another involved study which time did not permit. Monochloramine is the best oxidant available for reoxidation of the iodide ion in water distribution systems at present.

Table 42

Inorganic Oxidants Tested for Release of I<sub>2</sub> from I<sup>-</sup> in Water Distribution Systems

Compound	Formula	Test Temperature °C	pH Range	I <sub>2</sub> Concentrations	Oxidant Concentrations	Results
Potassium persulfate	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	23	7 - 9.5	1 - 5	1 - 5	Negative
Sodium persulfate	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	23	7 - 9.5	1 - 5	1 - 5	Negative
Potassiumperoxymono-sulfate (oxone)	KHSO <sub>5</sub> -KHSO <sub>4</sub> -K <sub>2</sub> SO <sub>4</sub>	23	7 - 9.5	1 - 5	1 - 5	Positive
Sodium borate tetrhydrate	NaBO <sub>3</sub> · 4H <sub>2</sub> O	23	7 - 9.5	1 - 5	1 - 5	Negative
Sodium borate perhydrate	NaBO <sub>3</sub> · H <sub>2</sub> O	23	7 - 9.5	1 - 5	1 - 5	Negative
Ammonium persulfate	(NH <sub>4</sub> )S <sub>2</sub> O <sub>8</sub>	23	7 - 9.5	1 - 5	1 - 5	Negative
Calcium peroxide	CaO <sub>2</sub>	23	7 - 9.5	1 - 5	1 - 5	Negative
Zinc peroxide	ZnO <sub>2</sub>	23	7 - 9.5	1 - 5	1 - 5	Negative
Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	23	7 - 9.5	1 - 5	1 - 5	Negative
Chlorine	Ca(OCl) <sub>2</sub>	23	7 - 9.5	1 - 5	1 - 5	Positive
Monochloramine	NH <sub>2</sub> Cl	23	7 - 9.5	1 - 5	1 - 5	Positive

Negative indicates no release of I<sub>2</sub> from I<sup>-</sup> during the period of the test.Positive indicates release of I<sub>2</sub> from I<sup>-</sup> within the period of the test.All of the oxidants which failed to release I<sub>2</sub> from I<sup>-</sup> at pH values between 7.0 and 9.5 would release the I<sub>2</sub> from the I<sup>-</sup> at pH 5.0 and below.



## VI. SUMMARY

The water in two water systems supplying three Florida correctional institutions and serving a total of approximately 800 individuals has been continuously disinfected with iodine for a period of two years under carefully planned chemical, bacteriological and medical controls. To date 70 million gallons of water has been iodinated.

The physical and chemical properties of iodine make it particularly suitable for use as a water disinfectant. Since its vapor pressure is only 0.31 mm of Hg at 25°C, it may be stored indefinitely in nonmetallic containers and at atmospheric pressure without appreciable loss or deterioration. Although its water solubility is not high, its saturated solution is sufficiently concentrated for feeding purposes. Its low chemical reactivity, least of all the halogens, means that lower residuals are more stable and therefore persist longer in the presence of organic or other oxidizable materials, and the possibility of the production of tastes and odors by such reactions is minimized. The feeding of elemental iodine to water is a very simple procedure. No difficulties have been encountered in continuously feeding the element in saturated water solution to provide any desired dosage with an overall accuracy of plus or minus .05 parts per million.

Iodine has been shown to be extremely effective for the disinfection of two public water supplies. Of over 1000 samples collected from the two systems for bacteriological analysis during a 22 month

period of iodination, only about 2% were unsatisfactory, far lower than the number permissible by the 1962 DRINKING WATER STANDARDS. Disinfection was begun with a dosage of 1.00 parts per million but during three months of the study the dosage was only 0.30 parts per million.

One of each of four inmates in the three institutions, a total of 149 subjects, were selected for medical and physiological tests. The group included 45 adult white males, 20 white and colored adult females, and 34 colored girls. The series was completed by 67 subjects. Medical studies included the assessment of the three indices of thyroid function, namely, radioactive iodine uptake (RAI), protein bound iodine (PBI), and serum thyroxine ( $T_4$ ), and a study of urinary iodine excretion. Each subject received the series of tests twice before iodine feed was begun and 30 days apart, following which the tests were made on all subjects one, three, seven, and ten months after beginning the feed of iodine. Determinations were also made of the ratio of urinary iodide to creatinine excreted in each of 50 inmates. As might be expected the RAI intake dropped from about 17% at the beginning of the study to about 2% at the end. Values for PBI increased somewhat but the mean for the group was still within the range of values found in normal individuals. No significant change in the mean value for serum thyroxine was found. There has been no apparent change in the physical examination, and specifically no change in the size of the thyroid gland. No allergic reactions attributable to iodine have been found. There is no evidence to date that iodine under these experimental conditions has any detrimental effect on general health or

thyroid function.

In dosages up to 1.00 parts per million, iodine produces no discernible color, taste, or odor in water.

The relatively high cost of iodine compared to chlorine is offset by three important considerations. First, its low chemical reactivity is shown to result in low iodine demands even in the presence of gross pollution. Second, under actual conditions of use, little or no iodine is lost by iodate formation. Last, but most important, the ease with which the iodide ion may be reoxidized makes it possible to maintain disinfecting residuals to the furthest extremities of the distribution system by a choice of the proper oxidizing agent.

A swimming pool study was made to investigate the possibility that iodine may be absorbed by the skin of individuals exposed to water containing it. Twenty-two subjects received the same series of tests as those used at Lowell before and after swimming throughout a period of one month in pool water disinfected with iodine. Average values for the group for RAI, PBI and  $T_4$  were not significantly changed and no evidence of allergy or change in size of the thyroid gland was detected in any subject during the study.

Both iodine and chlorine, the latter having been evaluated in a preliminary base-line study, were shown to be effective agents in the concentration range 0.3 - 0.6 parts per million and at pH values between 7.3 - 7.6. Of 162 samples examined for coliform organisms during the iodination period, 155 or 95.7% were found to be free of coliforms, and 153 or 94.5% were free of enterococci. It is in the disinfection of swimming pool water that the ability to readily reoxidize and reuse

the iodide ion pays greatest dividends because calculations indicate that each atom of elemental iodine may be reoxidized and reused an average of 10-13 times before being lost. In this study a careful record was kept of all chemicals used for disinfection and pH control and accurate data covering chlorine disinfection were available. It was found that whereas the cost of chlorine disinfection had averaged \$7.98 per day, the cost for disinfection with iodine was only \$4.70 per day. Had it been possible to use sodium iodide rather than potassium iodide, the cost would have been reduced to \$3.72 per day. Amazing as it may seem, it is possible to disinfect swimming pool water with iodine at a cost of approximately half that of chlorine, even though elemental iodine costs approximately \$1.16 per pound, and chlorine in 150 pound cylinders in the range of 10-12 cents per pound.

A comparison of the chlorine and iodine demands of Lowell water to which a number of organic compounds of different types, industrial pollutants and domestic sewage were added, indicated, as would be expected, that whereas the reaction of chlorine with these materials is rapid, that of iodine is much slower and in some important cases, such as with  $\text{NH}_3$  and phenol, there is no reaction.

Preliminary quantitative studies of the effect of iodine, both dry and in aqueous solution, has indicated that a number of commonly available materials of construction are sufficiently resistant to its attack to be suitable for the construction of iodine feeders and discharge lines.

These studies indicate that iodine is fully as effective as

chlorine for the disinfection of public water supplies and that it possesses a number of advantages over chlorine when used for that purpose.

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## BIOGRAPHICAL SKETCH

Riley Nelson Kinman was born in Dry Ridge, Kentucky, on January 25, 1936. In 1954 he graduated from Dixie Heights High School of Edgewood, Kentucky. He attended the University of Kentucky from 1954 to 1959 where he received his Bachelor of Science degree in Civil Engineering.

After serving six months of active duty in the Army as a Second Lieutenant, he was an engineer for the city of Dayton, Ohio Water Department, supervising the design, construction, operation, and testing of water and sewage facilities.

In September, 1961, he entered the University of Cincinnati as a Public Health Service Engineering Trainee and received his Master of Science degree in August, 1962. His research for this degree was a quantitative study of water stability, part of which was carried on full-scale with the water treatment plant at Dayton.

In January, 1963, Mr. Kinman enrolled in the Graduate School of the University of Florida for the purpose of earning his doctorate degree. From August, 1965 to date he has been a research associate in the Department of Chemistry. As a result of this graduate work he has already published three papers on the disinfection of water with iodine.

Mr. Kinman is married to the former Barbara JoCeil Brown of Lexington, Kentucky, and is the father of a son and daughter.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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